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16. ABSTRACT

This report describes research on the determination of the equilibrium fluoride adsorption capacity of small columns of acid pretreated activated alumina (Alcoa F-1 grade). The experimental observations verified the expectation that fluoride is very favorably adsorbed in preference to the common anions: sulfate, chloride and bicarbonate. However, the adsorption capacities were found to be four to five times higher than what has been reported in the early literature for municipal defluoridation processes.

Fluoride adsorption capacity is significantly affected and is decreased with an increase in pH beyond seven. The alumina selectivity sequence determined by experiments was the same as has been reported in the early literature, $OH^- > F^- > SO_4^= > Cl^- > HCO_3^-$. Although fluoride anions are preferred over sulfate ions, the sulfate ions compete significantly at the levels found in ground water supplies. Experiments with high ionic strength ranging up to 56 millimoles per liter (5600 ppm as $CaCO_3$) indicate that the total adsorption capacity increases slightly. Fluoride adsorption capacity decreases only slightly with the very significant increases in the concentrations of the other anions. These equilibrium data will prove useful in utilizing the maximum adsorption capacity of activated alumina in municipal defluoridation processes.

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THE EQUILIBRIUM FLUORIDE CAPACITY OF ACTIVATED ALUMINA

Determination of the Effects of pH and Competing Ions

by

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

Pursuant to the provisions of the Safe Drinking Water Act of 1974 (Public Law 93-523), many public water supplies in the U.S. may eventually have to be treated to remove excess fluoride. The research described in this report establishes the maximum adsorption capacity of activated alumina for the removal of fluoride ions as influenced by pH and competing ions, viz., sulfate, chloride, and bicarbonate.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

This report describes research on the determination of the equilibrium fluoride adsorption capacity of small columns of acid-pretreated activated alumina (Alcoa F-1 grade). Mini-columns containing 1 g alumina adsorbent were equilibrated over a period of 6 to 10 days with continuous flows of constant pH fluoride solution. The adsorbed ions were then eluted with 1% sodium hydroxide solution over a period of 4 hours. The alkaline regenerants were analyzed to determine the quantities of ions "adsorbed" (ion exchanged) during the exhaustion step. As expected, fluoride was very favorably adsorbed compared to the common anions: sulfate, chloride, and bicarbonate. However, the equilibrium fluoride adsorption capacity was found to be twice as great as that reported in the recent literature for municipal defluoridation processes.

Fluoride adsorption capacity is significantly affected and is decreased with an increase in pH beyond 7. The alumina selectivity sequence determined by experiments was the same as has been reported in the early literature: $OH^- > F^- > SO_4^= > Cl^- > HCO_3^-$. Although fluoride ions are preferred over sulfate ions, the sulfate ions compete significantly at the levels found in groundwater supplies. Fluoride adsorption capacity decreases only slightly with the very significant increases (up to 56 millimoles/L) in the concentrations of the other anions.

The laboratory research on fluoride removal was done in support of field studies on the removal of fluoride using activated alumina columns in a mobile pilot plant designed and constructed at the University of Houston. The Mobile Drinking Water Treatment Research Facility was completed on April 9, 1980, and transported to its first field location—Taylor, Texas, a small community (population 13,000) with a high-fluoride (3.0 mg/l) groundwater supply. The mobile facility containing activated alumina and ion exchange columns and reverse osmosis and electrodialysis units may be transported to any U.S. community with an inorganic contaminant problem.

This report is submitted in partial fulfillment of Grant Number R8 06073-010 by the University of Houston under the sponsorship of the U.S. Environmental Protection Agency. A second project report covering the design, construction, and operation of the Mobile Drinking Water Treatment Research Facility will be published at a later date.

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LIST OF ABBREVIATIONS AND SYMBOLS

α_A^B	Separation factor between ions B and A, dimensionless
BV	Bed volume
b_i	Langmuir constant related to adsorption energy, l/mg
C_e	Liquid phase concentration, mg anion/l
EBCT	Empty Bed Contact Time
I	Ionic strength, moles/liter
K	Freundlich constant, mg/g
M	Moles
n	Freundlich constant, g/l
Q	Rate of flow through column, ml/min
Q'	Langmuir ultimate solid phase adsorption capacity constant, mg/g
q_e	Solid phase concentration, mg anions adsorbed/gm Al
r	Correlation coefficient
$t_{.9}$	Time in hours to reach 90 percent equilibrium of exhausting mini-column
T	Throughput, i.e., ratio of the total amount of fluoride which comes in contact with the adsorption column during a specified amount of time to the total adsorptive capacity of the column
$T_{.9}$	Throughput at 90 percent approach to equilibrium
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon

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SECTION 1

INTRODUCTION

EFFECTS OF FLUORIDE IN DRINKING WATER

Chronic effects of fluoride on the skeletal system have been documented in several geographic areas where drinking water contains excessive fluoride. This form of chronic fluorosis was first described in India and has since been reported in Ceylon, China, South Africa, Japan, Saudia Arabia, the United States, Canada, and Europe [W.H.O., 1970].

Mottled tooth enamel is the most delicate index of chronic fluorosis in humans. It is epidemic in areas where the drinking water contains 2 ppm F^- or more, and there is a precise relationship between the severity of mottling and the concentration of fluoride in the drinking water [Sognnaes, 1953]. In a 1953 report on the medical aspects of fluorosis in Bartlett, Texas, where the drinking water contained 8 ppm of fluoride [Shimkin, et al., 1953], a little difference was discovered between the "high fluoride" group and the control group with respect to the number and types of specific disease symptoms elicited. However, the high fluoride group manifested a higher incidence of mottled enamel and an increased bone density of the spine and pelvis. They also experienced a certain brittleness and blotching of the fingernails, hypertrophic changes in the spine and pelvis, and lenticular opacities in the eye.

Dental tissues (including the skeleton) accumulate fluoride most rapidly during formation and mineralization [National Research Council, 1971]. During tooth formation, the cells of the dental tissues—particularly ameloblasts—are very sensitive to fluoride. At relatively low doses (e.g., 2 ppm of fluoride in the water) small spots of discoloration may form in the tooth surface. These spots, or "mottling," vary in color from paper white to dark brown, the brown stains usually accumulating when exposure to fluoride persists after the tooth has erupted. At higher doses, the cells may be affected and the tooth structure severely altered, so that the normally smooth surface becomes corrugated.

The effects of fluoride in drinking water on animals are analogous to those in human beings. The ingestion of excessive amounts of fluoride by young farm animals for long periods causes striking changes in the teeth such as brown discolorations, pitting, and marked wear of the entire tooth. The exposure of adult farm animals with completely erupted teeth to excessive amounts of fluoride for long periods will produce chronic symptions of fluorosis, except that the teeth will remain smooth. Bones and joints of animals

may become enlarged, and extra bone growths or extroses may appear in different parts of the skeleton. Some animals may become stiff, and intermittent lameness may occur [Greenwood, 1956].

MAXIMUM CONTAMINANT LIMITS FOR FLUORIDE

The U.S. Public Health Service (USPHS) Drinking Water Standards of 1962 set a mandatory limit for fluoride based on the annual average of maximum daily ambient temperature. The fluoride-temperature relationship has been established on the premise that the consumption of water increases with temperature; therefore, the maximum allowable fluoride levels should decrease with increased temperature. The U.S. Environmental Protection Agency (U.S. EPA) subsequently adopted these standards [Federal Register, 1975] (Table 1) when promulgating the National Interim Primary Drinking Water Regulation (NIPDWR) pursuant to the Safe Drinking Water Act (PL 93-523).

In May 1972, the National Institute of Dental Research estimated that community public water supply systems serving approximately 4.2 million people exceeded the recommended maximum contaminant levels established for fluoride. A summary published in January 1980 revealed that in the state of Texas, over 400 community water supplies exceeded their maximum NIPDWR limit of 1.6 mg/l of fluoride.

FLUORIDE REMOVAL PROCESSES

Several methods of defluoridation have been utilized for municipal and residential fluoride removal. These methods can be broadly categorized into two kinds of processes: (1) precipitation methods and (2) packed bed adsorption methods.

In the first category, chemicals like lime (alone or in combination with magnesium from dolomite), magnesium sulfate, magnesia, or calcium phosphate are added to precipitate fluoride or to form hydroxide precipitates onto which fluoride will adsorb and settle out of solution. Addition of other chemicals —such as bentonites, fuller's earth, diatomaceous earth, silica gel, bauxite, sodium silicate, sodium aluminate, and ferric salts—has also been attempted, but these materials require a very low pH (less than 3.0) to effect fluoride removal in reasonable quantities.

When both hardness and fluoride removal are desired and the water contains sufficient magnesium, softening is the most feasible process. On the other hand, fluoride removal with alum has been found to require three to five times the usual alum dose of 50 ppm normally required for water clarification. At LaCrosse, Kansas, raw water was treated with 225 ppm of alum to reduce the fluoride content from 3.6 to 1.5 ppm [Culp and Stoltenberg, 1958]. Maier [1953] reported that water treatment at Bartlett would have required 900 ppm alum to remove 7 ppm fluoride, and further dosage would have raised the sulfate content to a very undesirable level. Thus the total costs of alum treatment of groundwater, including sludge disposal, would likely be prohibitive for most small communities. Furthermore, when fluoride is the only contaminant

TABLE 1. MAXIMUM CONTAMINANT LEVELS (MCLs) FOR FLUORIDE
(From National Interim Primary Drinking Water Standards, 1975)

Average Maximum Daily Temperature		
Temperature °F	Temperature °C	MCL mg/1
53.7 and Below	12.0 and Below	2.4
53.8 to 58.3	12.1 to 14.6	2.2
58.4 to 63.8	14.7 to 17.6	2.0
63.9 to 70.6	17.7 to 21.4	1.8
70.7 to 79.2	21.5 to 26.2	1.6
79.3 to 90.5	26.3 to 32.5	1.4

whose removal from drinking water is required, neither alum nor lime addition may prove economical.

When fluoride alone must be removed from drinking water, fluoride adsorption on activated alumina, bone char or tricalcium phosphate has historically been considered the most reasonable, cost-effective removal method [Clifford, 1978]. However, an unanswered question remains as to which media is superior overall for fluoride removal when capacity, service life, regenerant requirements, and media cost are taken into consideration.

Much confusion exists in the literature regarding the fluoride capacities of the various media. The reason for this confusion can be attributed to the fact that the fluoride capacity of an adsorbent depends rather heavily on (1) the pH of the feedwater and (2) the regeneration history of the adsorbent. In addition, competing anions and cations and the total ionic strength of the feedwater are expected to influence the fluoride adsorption or ion exchange process. In general, one or more of these significant parameters have been overlooked by earlier investigators [Fink and Lindsay, 1936; Swope and Hess, 1937; Savinelli and Black, 1958].

Clifford [1978] has collected and summarized data from municipal defluoridation installations dating back to 1937. This data are reproduced below as Table 2.

TABLE 2. FULL-SCALE PACKED-BED DEFLUORIDATION PLANTS

Process, Location, Date, (Reference)	Gross Installed Capacity MGD	Process Description and Operation
Tri Calcium Phosphate Climax, CO, 1937 (Wamsley & Jones, 1947)	0.304	Regeneration with NaOH then CO_2 neutralization Regeneration operation considered complicated and time consuming F^- removal operates "esceptionally well" No mention of attrition losses
Bone Char Briton, SD, 1948 (Maier, 1953)	0.30	Bone char replaced original "Fluorex," $Ca_3(PO_4)_2$, media Fluorex losses were 42 percent/year Regeneration with NaOH, then CO_2 neutralization In 1960, this was the only F^- plant still using bone char Plant abondoned in 1971
Activated Alumina Bartlett, TX, 1952 (Maier, 1953, 1970)	0.58	Regeneration with NaOH then H_2SO_4 neutralization F^- level = 0.5 - 2.0 ppm in plant effluent Alkalinity, hardness, pH, SO_4^{2-}, and F^- all variable in effluent F^- concentration in raw water determines F^- capacity of alumina Plant abandoned in 1977
Bone Char Ft. Irwin, CA, 1954 (Harmon, 1965)	0.095	Regeneration with NaOH, neutralization with H_3PO_4 Semi-automatic regeneration triggered by manual grab samples F^- removal capacity decreases with each regeneration Media had to be replaced annually
Tri Calcium Phosphate Apple Valley, CA, 1961 (Harmon, 1965)	0.144	Regeneration with NaOH, then CO_2 neutralization Spent regenerant disposal by evaporation pond $Ca_3(PO_4)_2$ fines in treated water Initially high attrition losses, later insignificant
Activated Alumina Elsinor, CA, 1960 (Harmon, 1965)	0.72	Regeneration with NaOH then H_2SO_4 neutralization "Fortunately" treatment didn't remove H_2S Pretreatment = lower pH from 9.9 to 7.4 Alumina "cementation" problem encountered Abandoned after only a few years of operation Replaced by a low F^- supply

TABLE 2. FULL-SCALE PACKED-BED DEFLUORIDATION PLANTS
(Continued)

Process, Location, Date (Reference)	Gross Installed Capacity MGD	Process Description and Operation
Activated Alumina Gila Bend, AZ, 1978 (Rubel and Woosley, 1979)	0.75	Raw water pH adjusted to pH 5.5 Regeneration done in two steps Upflow and downflow rinses with 1% NaOH solution followed by neutralization with 2.5 pH adjusted raw water Removal capacity observed 2000 grains/ft^3

SECTION 2

CONCLUSIONS

From these equilibrium experiments it can be concluded that the adsorption of fluoride onto activated alumina is a function of pH, and that the optimum pH for adsorption ranges between 5.0 and 6.0. While early literature reported maximum fluoride adsorption capacities from 0.95 to 2.3 mg fluoride/gm alumina, at these optimum conditions, fluoride adsorption capacity reached 10.1 mg fluoride/gm alumina at 6 ppm fluoride in the water. The pure-fluoride equilibrum capacities found in these experiments are 20 to 50% higher than the best column capacities reported in the literature. The differences are thought to be due to kinetic limitations and sulfate competition in actual defluoridation processes utilizing packed beds of activated alumina.

The experimentally determined selectivity sequence was identical to that reported in the literature, viz, (in order of preference):

$$OH^- >> F^- >> SO_4^{2-} >> Cl^- > HCO_3^-$$

Fluoride adsorption capacity was not significantly reduced by substantial increases in total dissolved solids concentration, except when sulfate was present. Sulfate competition from (from 250 mg/l SO_4^{2-}) will reduce the equilibrium fluoride adsorption capacity of activated alumina by as much as 25% when pH = 7.1 and F^- = 5.7 mg/l.

Indications are that the rate of fluoride adsorption on alumina increases as pH increases especially in the pH range of 6 - 8.

SECTION 3

THEORY

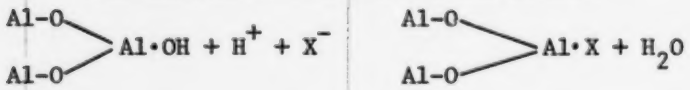
ACTIVATED ALUMINA

"Activated alumina" is the common name for gamma aluminum oxide (γ-Al_2O_3), a porous adsorbent with a moderately high BET surface area (150 - 300 m^2/g). It adsorbs liquids and gases without changing form. It is manufactured by low temperature dehydration at 300 - 700°C of hydrous aluminum oxide, and differs from high temperature alpha alumina (α-Al_2O_3) in that it readily takes up water and dissolves in acids (both forms are soluble in strong alkalis). Activated aluminas are used as adsorbents in a variety of processes, principally to dehydrate organic liquids and gases. Gamma activated alumina was one of the earliest adsorbents used in inorganic ion chromatography [Kubli, 1947]. It was then known to be quite specific for hydroxide, fluoride, phosphate, and silicate.

ADSORPTION

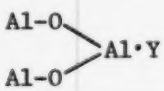
Activated alumina is usually grouped with silica, magnesia, and molecular sieves as a "polar adsorbent." Its crystal structure is that of defect spinel ($MgAl_2O_4$) and contains cation lattice discontinuities giving rise to localized areas of negative charge. Since electroneutrality considerations mandate the balancing presence of areas of positive charge, sites for both cation and anion adsorption are available [Clifford et al., 1978]. In an experiment of nitrobenzene adsorption on activated alumina, Hesse and Sauter hypothesized that both the mechanism of "van der Waals" adsorption and ion exchange adsorption (i.e., salt transformation through the exchange of one ion for another) occur, and that nitrobenzene is bound on surface locations which are not affected by pH change. Kubli [1947] reported that the most important factors affecting ion exchange adsorption are the nature of the pretreatment and the quantity of mostly inorganic acids or bases in the alumina, while such factors as grain size and drying temperature are of minor importance. He reported that the anion adsorption behavior of alumina treated with the base, Na_2CO_3, was due to the precipitation of metal carbonates or hydroxides and that anion adsorption behavior depended on pretreatment with an acid such as HCl or $HClO_4$. He proposed the following mechanisms for anion exchange on alumina.

Adsorption-Neutralization of Acid HX

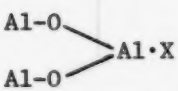


Exchange of Preferred Ion Y^- for X^-

The above mechanism can take place when the solubility of



is lower than



REGENERATION

According to Kubli, the elution of adsorbed ions from the column (regeneration) can be accomplished by three different means:

1. By alkali elution (reversal of the column)

2. By elution with anions which form less soluble basic aluminum salts

3. By higher concentration of the anions originally bound to the column

Kubli also expanded the selectivity sequence of anion adsorption on alumina originally established by Schwalb and Dattler [1937]. The sequence of important anions in the expanded series is as follows:

$$OH^- \gg PO_4^{3-} \gg F^- \gg SO_4^{2-} \gg Cl^- \gg NO_3^-$$

Clifford et al [1978] have suggested a simplified series of chemical reactions to explain the ion exchange adsorption of fluoride and the subsequent regeneration of the packed bed of fluoride-exhausted alumina:

SIMPLIFIED PICTURE OF ALUMINA
ADSORPTION AND REGENERATION REACTIONS

1. NEUTRAL ALUMINA

$$\text{Alumina} + HOH \longrightarrow \text{Alumina}\cdot HOH$$

2. ACIDIFICATION

$$\text{Alumina}\cdot HOH + HCl \longrightarrow \text{Alumina}\cdot HCl + HOH$$

3. ION EXCHANGE IN ACIDIC SOLUTION

$$\text{Alumina}\cdot HCl + NaF \longrightarrow \text{Alumina}\cdot HF + NaCl$$

4. REGENERATION

$$\text{Alumina}\cdot HF + 2NaOH \longrightarrow \text{Alumina}\cdot NaOH + NaF + HOH$$

5. ACIDIFICATION

$$\text{Alumina}\cdot NaOH + 2HCl \longrightarrow \text{Alumina}\cdot HCl + NaCl + HOH$$

CHARGE DEPENDENCE

Many researchers in the fields of soil and minerology have studied the presence of electric charges on the oxide minerals suspended in aqueous solutions. These charges comprise an important consideration when determining the extent to which the solids to which they are attached can function as adsorbents in ion exchange columns [Amphlett, 1964; Bolt, 1965; Van Olphen, 1963]. The isoelectric point IEP (s) and the zero point of charge (ZPC) are convenient references for predicting charge dependence behaviors [Parks, 1967].

Parks defined the ZPC as the pH at which solid surface charge from all sources is zero. The IEP(s) is a ZPC arising from the interaction of the solid with H^+ and OH^-, i.e., the interaction of the solid with water. For other species, the ZPC will vary with the ionic composition of the system. Data on pH_{IEPs} and pH_{ZPC} for most minerals [Parks, 1965] are available elsewhere. Values for the pH_{IEPs} of activated alumina have been determined [Choi, 1979] and are presented in Table 3; aging in DI water raises the pHIEPs.

In general, the sign of the surface charge itself will determine the anionic or cationic adsorption behavior. Thus aluminum oxide may be either a cation exchanger (in alkaline medium) or an anion exchanger (in acid medium), and within a certain pH range, can act as an amphoteric ion exchanger [Zhabrova, 1961]. While surface charge is by no means the only factor responsible for electrolyte adsorption, the extent of adsorption decreases rapidly when the sign of the oxide's surface charge is changed to that of the sorbing species. However, Umland [1959] pointed out that in cases where the removal of ions cannot be entirely attributed to either ion exchange or molecular sorption, it may be caused by the precipitation of sparingly soluble bases and basic salts.

By comparison, adsorption caused by electrostatic attraction alone can be considered non-specific or non-selective. Adsorption can also arise from

TABLE 3. ISOELECTRIC POINT OF ACTIVATED ALUMINA

Treatment	pH_{IEPs}
a. DI water wash, stored in DI water for two days	6.2
b. DI water wash, stored in DI water for seven days	5.8
c. DI water wash, 2N-HCl wash, followed by DI wash, stored in DI water for seven days	7.3
d. DI water wash, 2N-HCl wash, followed by DI wash, stored in DI water for ten days	8.9

electrostatic attraction augmented by hydrogen bonding, coordinate bonding, or London Van der Waals bonding. Adsorption under the combined influence of ionic and non-ionic bonding is called "specific adsorption," which can occur even when the surface is uncharged.

At ZPC, anion and cation adsorption is minimal [Parks, 1967]. Specific adsorption reverses the sign of the surface charge and shifts the ZPC [Hingston, 1972].

SECTION 4

METHODS AND MATERIALS

OBJECTIVES

Adsorption capacity of activated alumina for the fluoride ion is reported to be affected by pH [Fink and Lindsay, 1936], fluoride concentration [Maier, 1953], and the relative concentration of competing ions, especially sulfate [Kubli, 1947; Umland, 1956; Hess and Sauter, 1947; Rubel, 1979]. Nevertheless, the literature reveals that most studies of fluoride adsorption by alumina have been conducted either at uncontrolled pH values or in the presence of competing buffers, thus complicating interpretation of the results. In this report, experiments have been carried out specifically to determine, both quantitatively and qualitatively, the effect of numerous factors on fluoride concentration, competing ions, including sulfate, chloride, bicarbonate, and high ionic strength.

PROCEDURES

Conditioning the Alumina

1. A 200-ml sample of F-1 grade Alcoa activated alumina of mesh size 26-48, Lot 4630-18, was rinsed with water and decanted several times until all the suspended and fine particles were removed. (Typical properties of this product are shown in Table 4.)

2. The washed sample of alumina was trickled down into a 21-mm ID conditioning column (See Fig. 1B) containing deionized water, in such a way that no air bubbles remained or were entrapped in the settled alumina.

3. The column was eluted with tap water (which had been adjusted to pH 3) until the effluent pH dropped down to pH 5. The elution was concluded with tap water whose pH had been adjusted to exactly 5.0 with 0.01 N H_2SO_4 until equilibrium was attained at the column effluent.

4. The conditioned, acid-washed (pH 5) alumina was dried at 110°C in an oven for 48 hours.

Exhausting the Alumina with Standard F^- Solutions

1. 1.00 g of the dried conditioned alumina was placed in each of ten

TABLE 4. TYPICAL PROPERTIES AND SPECIFICATIONS OF ACTIVATED ALUMINA, F-1 TYPE

Constituents and Properties	Content
Al_2O_3	92.00%
Na_2O	0.90%
Fe_2O_3	0.08%
SiO_2	0.09%
Loss on ignition (1100°C)	6.50%
Form	Granular
Contact surface area (sq.m./g)	210
Size (mesh)	26 - 48
Bulk density loose (lb/ft^3)	52
Bulk density packed (lb/ft^3)	55
Specific gravity	3.3

11 mm ID standard wall pyrex mini-columns. No air bubbles were entrained in the settled alumina. See Fig. 1A.

2. The mini-columns were equilibrated by passing the standard fluoride solutions through them at an average flow of 0.5 - 4.0 ml/min. The effluent fluoride concentration was checked from time to time. It took from five to six days of continuous operation to achieve more than 90 percent equilibrium, i.e., the effluent F^- concentration $\geq$ 0.90 times influent F^- concentration. See Fig. 2 for typical mini-column set up.

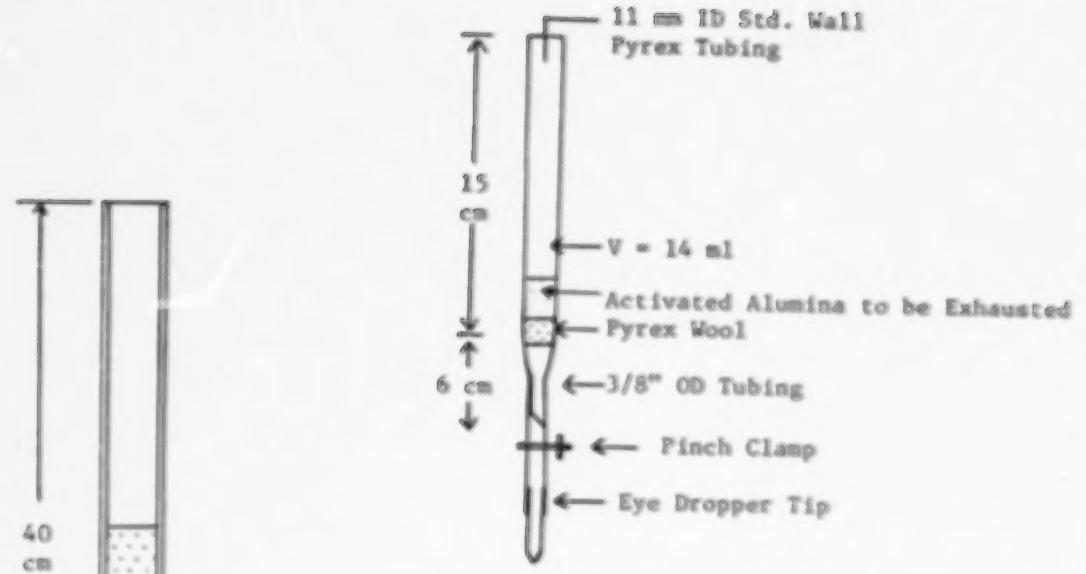
Regeneration of Fluoride-Spent Alumina

1. The equilibrated columns were disconnected and the solution in the columns drained to a point just above the surface of the alumina.

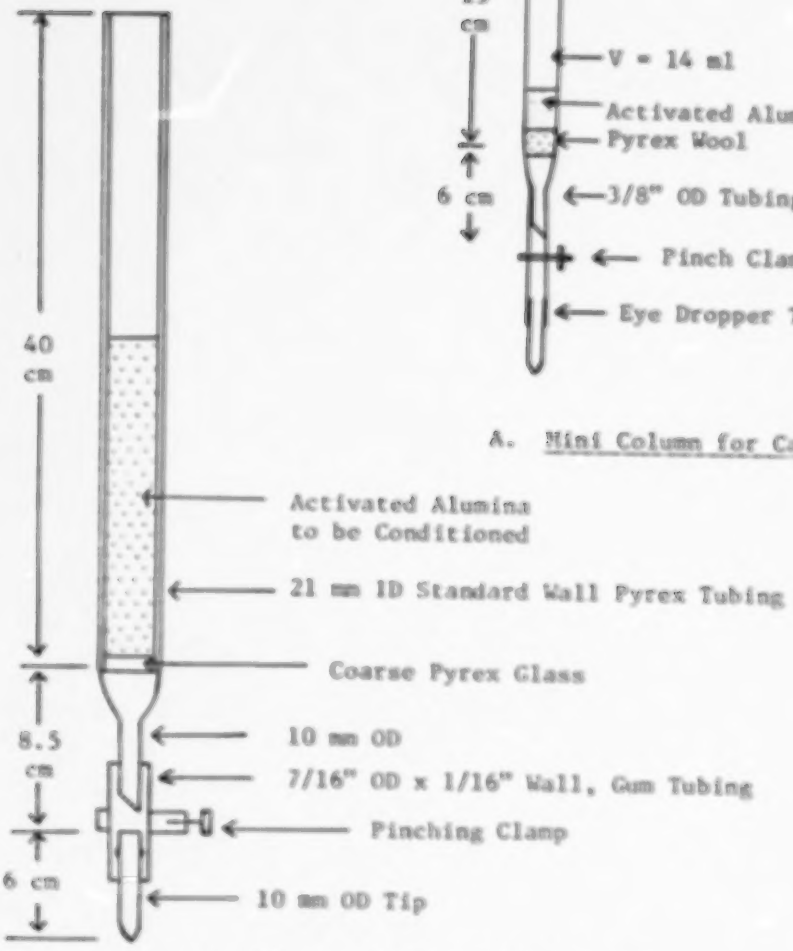
2. Each column was eluted with 100 ml one percent NaOH (.25 N) during a period of approximately four hours followed by 500 ml deionized water wash.

3. The regenerant solution was collected and diluted to exactly one liter.

NOTE: It had been previously determined that about 95 percent of the fluoride on the column could be recovered by this procedure.



A. Mini Column for Capacity Determination



B. Alumina Conditioning Column

Figure 1. A. Mini column for capacity determination.
B. Alumina conditioning column.

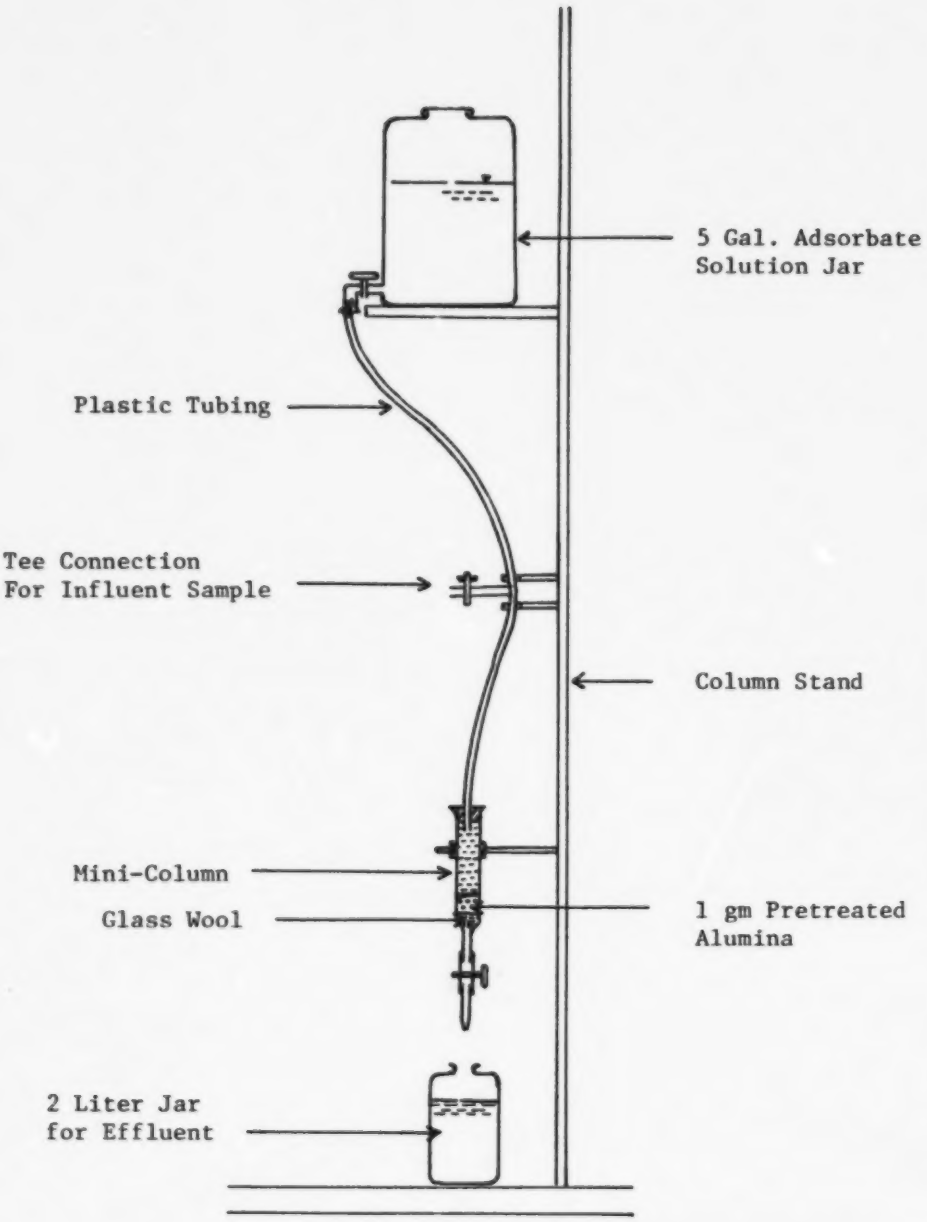


Figure 2. Typical Alumina Mini-Column Set Up for Adsorption Run
(Represents one of ten columns used simultaneously)

Analysis of Regenerant Solution

1. The regenerant solution was analyzed to determine the amounts of F^-, SO_4^{2-}, Cl^-, and HCO_3^- adsorbed on the alumina. The amount of fluoride adsorbed on the various alumina columns was thus determined as a function of pH, SO_4^{2-}, Cl^-, and HCO_3^- concentrations, and ionic strength.

METHODS AND MATERIALS

Feedwaters Used

pH-adjusted Houston tap water was used as a background solution for conditioning the alumina. Deionized water was used to make standard solutions which were passed through the alumina columns for the fluoride capacity determinations.

Fluoride Source

Sodium fluoride (reagent grade) was used to make standard fluoride stock solutions throughout the experiments.

pH Effects

To study pH effects on adsorption, influent fluoride standard solution was adjusted with diluted H_2SO_4 (for lowering the pH) or with diluted NaOH (for raising the pH). In addition, sodium carbonate solution was used as a buffer while preparing the standard fluoride solutions to maintain constant pH values of 7 and 8.

Standard Fluoride Concentrations Used

Fluoride concentrations of the standard solutions prepared with deionized water were diluted to 2.00, 4.00, 6.00, 8.00, and 10.00 mg F^-/1.

Concentrations of Competing Anions: SO_4^{2-}, Cl^-

To determine effects of competing ions, the fluoride concentration of all the standard solutions was kept fixed at .3 meq F^-/1 (5.7 mg F^-/1). The concentrations of competing ions used were 0.50, 1.00, 5.00, 10.0, and 15.0 meq/1 in the influent standard solution. The pH was fixed at 6.0 by adding 1 1/2 drops of N/20 NaOH for each two-liter solution.

High Ionic Strength Solutions

The high ionic strength standard solution consisted of Na^+, F^-, HCO_3^-, Cl^-, and SO_4^{2-} ions in deionized water. Some high ionic strength experiments were

run at pH = 7.1 and F^- = 0.3 meq/l (5.7 ppm) and others were run at pH = 7.1 and F^- = 0.5 meq/l (9.5 ppm). To produce the background ionic strength solutions, equivalent mixtures of Cl^-, HCO_3^-, and SO_4^{2-} were utilized to yield solutions of I = 3.8, 8.3, 14.3, 28.3, and 56.3 millimoles/liter.

See Tables 5, 6, and 7 for a complete analysis of the water for each experimental run.

TABLE 5. COLUMN DATA FOR DETERMINATION OF THE EFFECTS OF pH ON FLUORIDE ADSORPTION CAPACITY IN pH ADJUSTED DEIONIZED WATER SOLUTIONS

Run No*	Fluoride Concentration		Other Anions Present						Fluoride Capacity	
	mg/l	meq/l	pH	SO_4^{2-} meq/l	HCO_3^- meq/l	Q ml/min	$t_{.90}$ hrs	$T_{.9}$	mg F^-/g Al	meq F^-/g Al
1	2	.105	5.0	.005	-	4.18	104	6.29	8.27	.435
2	2	.105	5.0	.005	-	3.63	87.2	4.47	8.51	.448
3	4	.210	5.0	.005	-	2.13	90.5	4.67	9.85	.518
4	4	.210	5.0	.005	-	3.09	64.7	4.87	9.85	.518
5	6	.316	5.0	.005	-	4.01	24.9	3.31	10.89	.573
6	6	.316	5.0	.005	-	2.45	62.6	5.33	10.36	.545
7	8	.421	5.0	.005	-	3.54	33.0	5.34	10.49	.552
8	8	.421	5.0	.005	-	2.11	51.1	5.00	10.40	.547
9	10	.526	5.0	.005	-	3.91	21.3	4.75	10.53	.550
10	10	.526	5.0	.005	-	2.67	40.0	5.93	10.80	.570
11	2	.105	6.0	.006	-	.68	244	2.44	8.20	.431
12	2	.105	6.0	.006	-	.93	244	3.13	8.70	.458
13	4	.210	6.0	.006	-	.44	224	2.49	9.63	.507
14	4	.210	6.0	.006	-	.77	137	2.58	9.91	.521
15	6	.316	6.0	.006	-	.46	152	2.48	10.30	.542
16	6	.316	6.0	.006	-	.39	155	2.12	10.30	.537
17	8	.421	6.0	.006	-	.41	131	2.60	9.85	.518
18	8	.421	6.0	.006	-	.36	112	1.87	10.50	.553
19	10	.526	6.0	.006	-	.39	110	2.42	10.70	.563
20	10	.526	6.0	.006	-	.76	53.5	2.33	10.5	.553
21	2	.105	7.3	2.500	1.00	1.47	67.7	3.49	3.44	.181
22	4	.210	7.3	2.438	1.00	1.61	41.3	3.08	5.20	.274
23	6	.316	7.3	2.500	1.00	.83	52.1	2.50	6.25	.329
24	8	.421	7.3	2.500	1.00	1.44	30.1	2.96	7.03	.370
25	10	.526	7.3	2.250	1.00	.54	67.1	2.92	7.54	.397
26	2	.105	8.0	.625	1.00	.86	53.9	2.28	2.45	.129
27	4	.210	8.0	.625	1.00	1.46	27.2	2.58	3.72	.196
28	6	.316	8.0	.500	1.00	1.63	19.3	2.62	4.35	.229
29	8	.421	8.0	.687	1.00	1.39	26.3	2.65	4.82	.254
30	10	.526	8.0	.812	1.00	.83	31.9	3.03	5.28	.278

* A "run" is the exhaustion of one single column

1 meq/l SO_4^{2-} = 48 mg/l SO_4^{2-} = 50 mg/l as $CaCO_3$ 1 meq/l HCO_3^- = 61 mg/l HCO_3^- = 50 mg/l as $CaCO_3$

TABLE 6. COLUMN DATA FOR DETERMINATION OF THE EFFECTS OF SULFATE AND CHLORIDE ON FLUORIDE ADSORPTION CAPACITY AND α_i^F AT pH = 6.

Run No.	Q ml/min	$t_{.9}$ hrs	$T_{.9}$	Liquid Phase Concentration SO_4^{2-} meq/l	Liquid Phase Concentration Cl^- meq/l	Solid Phase Concentration F^- meq/l	Solid Phase Concentration SO_4^{2-} meq/l	Total	α_i^F
15	.46	152.0	2.48	.006	-	.542	.002	.544	.208
31	.89	104.0	3.69	.5	-	.454	.106	.560	7.14
32	.78	96.3	2.99	1.0	-	.451	.133	.584	11.4
33	.72	85.4	3.85	5.0	-	.390	.290	.680	22.4
34	1.66	34.1	2.74	10.0	-	.371	.246	.617	50.2
35	1.57	36.1	3.02	15.0		.367	.320	.687	57.34
							Cl^- meq/l		
36	.88	75.7	2.21	-	.5	.542	0.047	.589	19.2
37	.99	66.8	2.11	-	1.0	.568	0.003	.571	631
38	.59	111.0	2.13	-	5.0	.563	0.069	.632	136
39	.84	79.1	2.19	-	10.0	.547	0.034	.581	264
40	.62	107.0	2.07	-	15.0	.578	0.073	.651	545

NOTES:

1. A run is the exhaustion of one single column.
2. For runs 31 - 40, F^- concentration = 5.7 mg/1 (.300 meq/1).
3. For run 15, F^- concentration = 6.0 mg/1 (0.316 meq/1).
4. α_i^F = separation factor of F/Cl or F/SO_4. See Appendix for calculation.

TABLE 7. COLUMN DATA FOR DETERMINATION OF THE EFFECTS OF IONIC STRENGTH ON FLUORIDE ADSORPTION CAPACITY AT pH = 7.1

Run No. *	Fluoride Concentration mg F^-/l	Fluoride Concentration meq F^-/l	pH	Other Anions Present SO_4^{2-} meq/l	Other Anions Present Cl^- meq/l	Other Anions Present HCO_3^- meq/l	I mmoles/l	Q ml/min	$T_{.9}$	$t_{.9}$	Fluoride Capacity mgF^-/g Al	Fluoride Capacity meqF^-/g Al
41	5.7	.3	7.1	1.0	1.0	1.0	3.8	1.22	4.38	75.06	7.16	.377
42	5.7	.3	7.1	2.0	2.0	2.0	8.3	.78	3.95	106.69	7.21	.379
43	5.7	.3	7.1	4.0	4.0	4.0	14.3	1.27	3.63	56.11	6.76	.356
44	5.7	.3	7.1	8.0	8.0	8.0	28.3	.76	3.48	87.68	6.55	.345
45	5.7	.3	7.1	16.0	16.0	16.0	56.3	1.11	3.61	54.22	5.68	.299
46	9.5	.5	7.1	1.0	1.0	1.0	4.0	1.21	3.48	43.97	8.73	.459
47	9.5	.5	7.1	2.0	2.0	2.0	8.5	.75	3.71	68.45	7.94	.418
48	9.5	.5	7.1	4.0	4.0	4.0	14.5	.72	3.60	69.21	7.91	.416
49	9.5	.5	7.1	8.0	8.0	8.0	28.5	.90	3.24	48.00	7.62	.401
50	5.7	.5	7.1	16.0	16.0	16.0	56.5	1.22	2.93	29.97	7.13	.375

* A run is the exhaustion of one single column

SECTION 5

RESULTS

COLUMN EFFLUENT HISTORIES

Effluent fluoride concentration versus volume of feedwater, i.e., column effluent histories, were recorded for all the exhaustion experiments and are shown in Figs. A1 - A6. In the first two sets of early experiments (exhaustion of 20 columns), pairs of columns were run in an identical manner in order to check the precision of the results. The repeatability proved satisfactory.

The adsorption process for fluoride on activated alumina was observed to be very slow. It took over 120 hours to reach equilibrium. It has been further noted that the adsorption rate is relatively fast in the beginning and slowly decelerates to an asymptotic equilibrium. The area above the curves shows the accumulated fluoride adsorbed onto alumina. The effluent rate was not kept constant for any of the column pairs; to do so would have involved additional monitoring equipment, and the investigation of the kinetics of adsorption was not the primary intention of these tests. Nevertheless, the rate of flow was recorded for each column, and is depicted in column data, Tables 5 to 7.

EFFECT OF FLUORIDE CONCENTRATION

Results indicate that solid phase adsorption capacity is dependent upon the concentration of adsorbate in solution. Adsorption capacity increases with adsorbate concentration, while the rate of increase in adsorption capacity at lower concentrations is much higher than the rate of increase at higher concentrations.

For the first four sets of experiments in which pH had been kept fixed at 5, 6, 7, or 8, the influent fluoride concentration for each column was kept at 2, 4, 6, 8, or 10 mg/1. Equilibrium fluoride concentration effects are revealed in adsorption isotherms (Figs. 3 to 6). As expected, the total fluoride adsorption capacity of alumina increased with increasing equilibrium fluoride concentration. Regarding the rate of adsorption, however, Figs. A1 - A6 illustrate that fluoride uptake slows down as available adsorption sites are filled. As equilibrium is approached, the number and availability of adsorption sites decrease thus the adsorption rate decreases.

The adsorption isotherms obtained are of the Langmuir type. Average

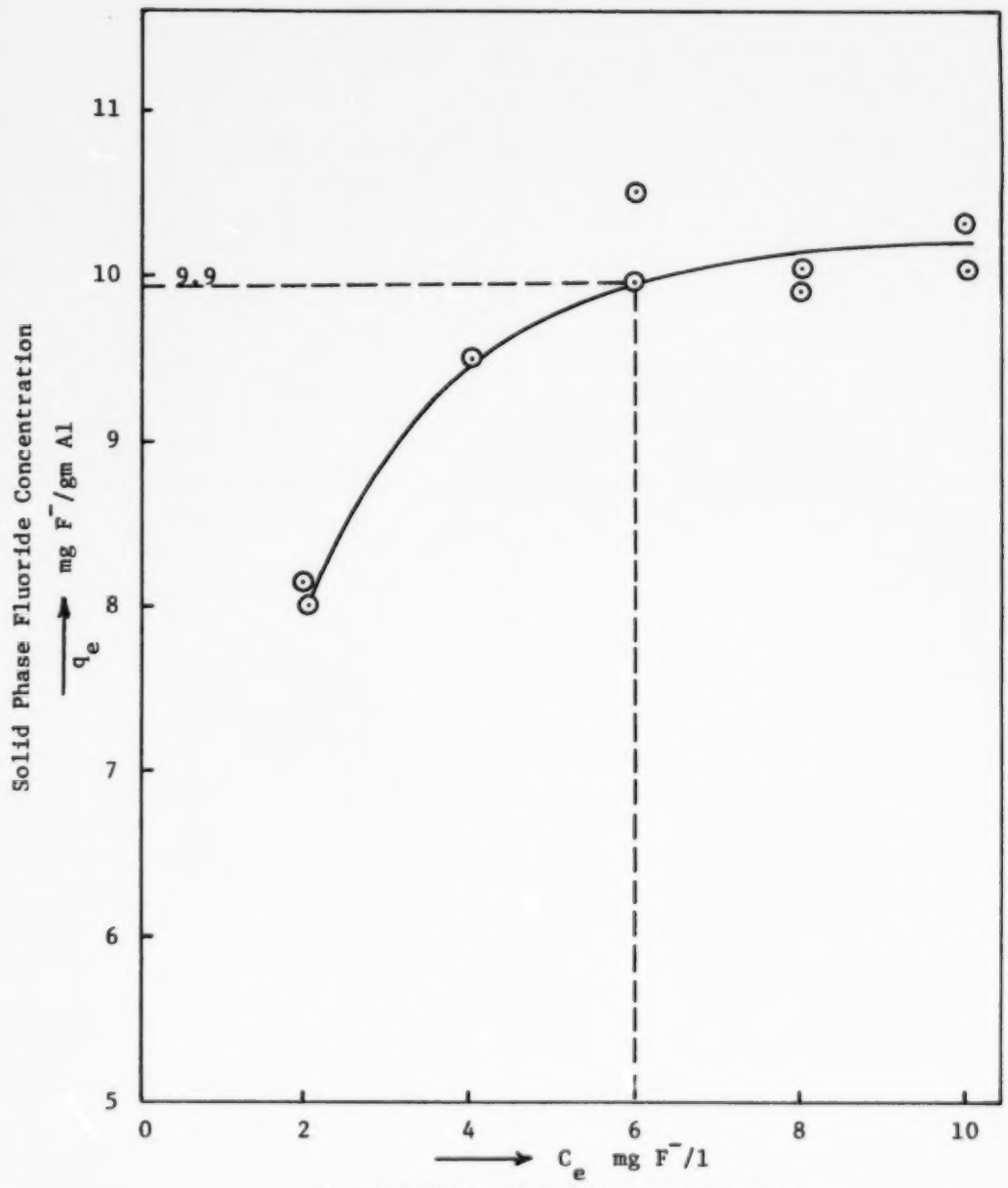


FIGURE 3. FLUORIDE ADSORPTION ISOTHERM

Adsorbate pH = 5.0, temperature = 22°C

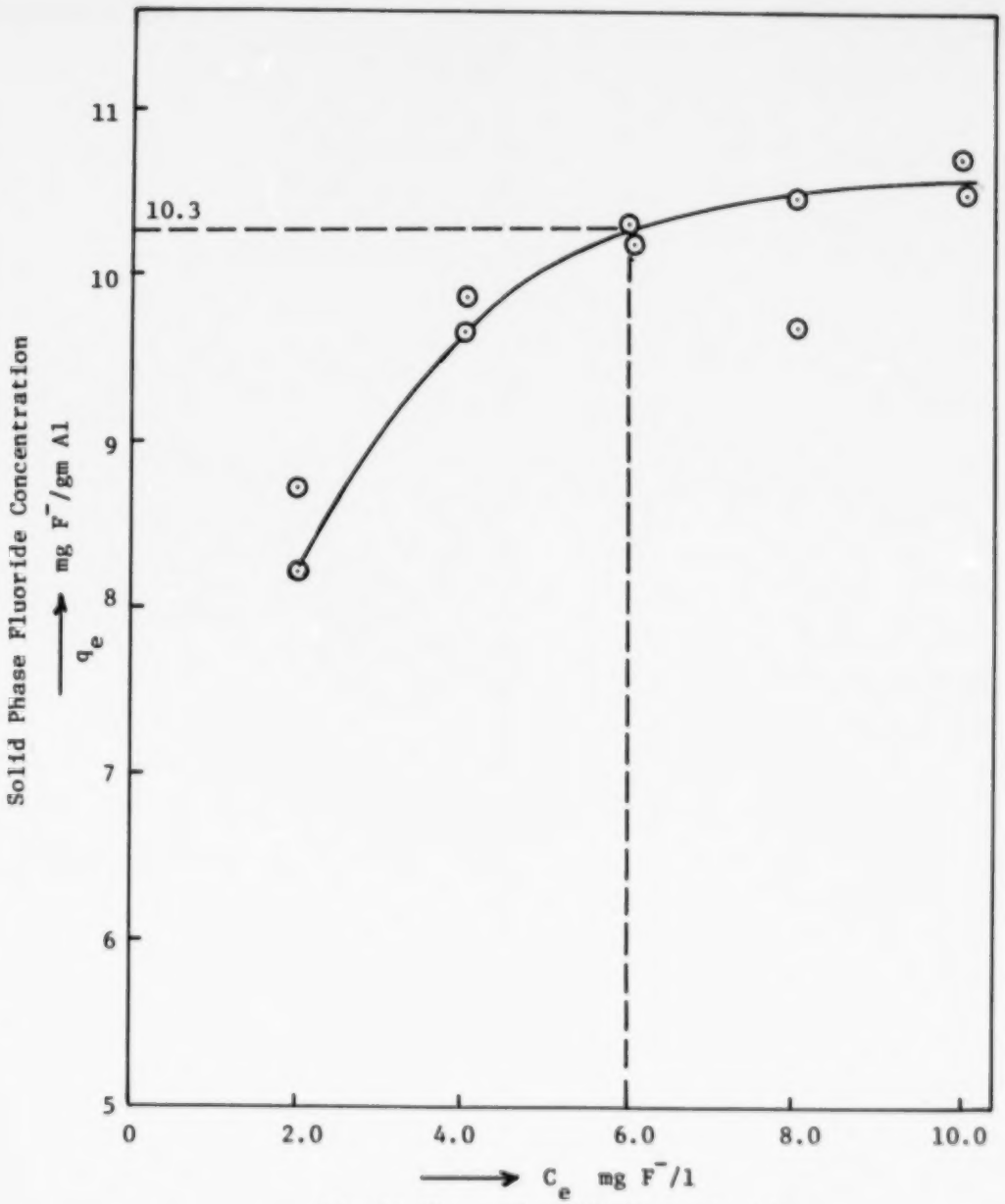


FIGURE 4. FLUORIDE ADSORPTION ISOTHERM

Adsorbate pH = 6.0, temperature = 22°C

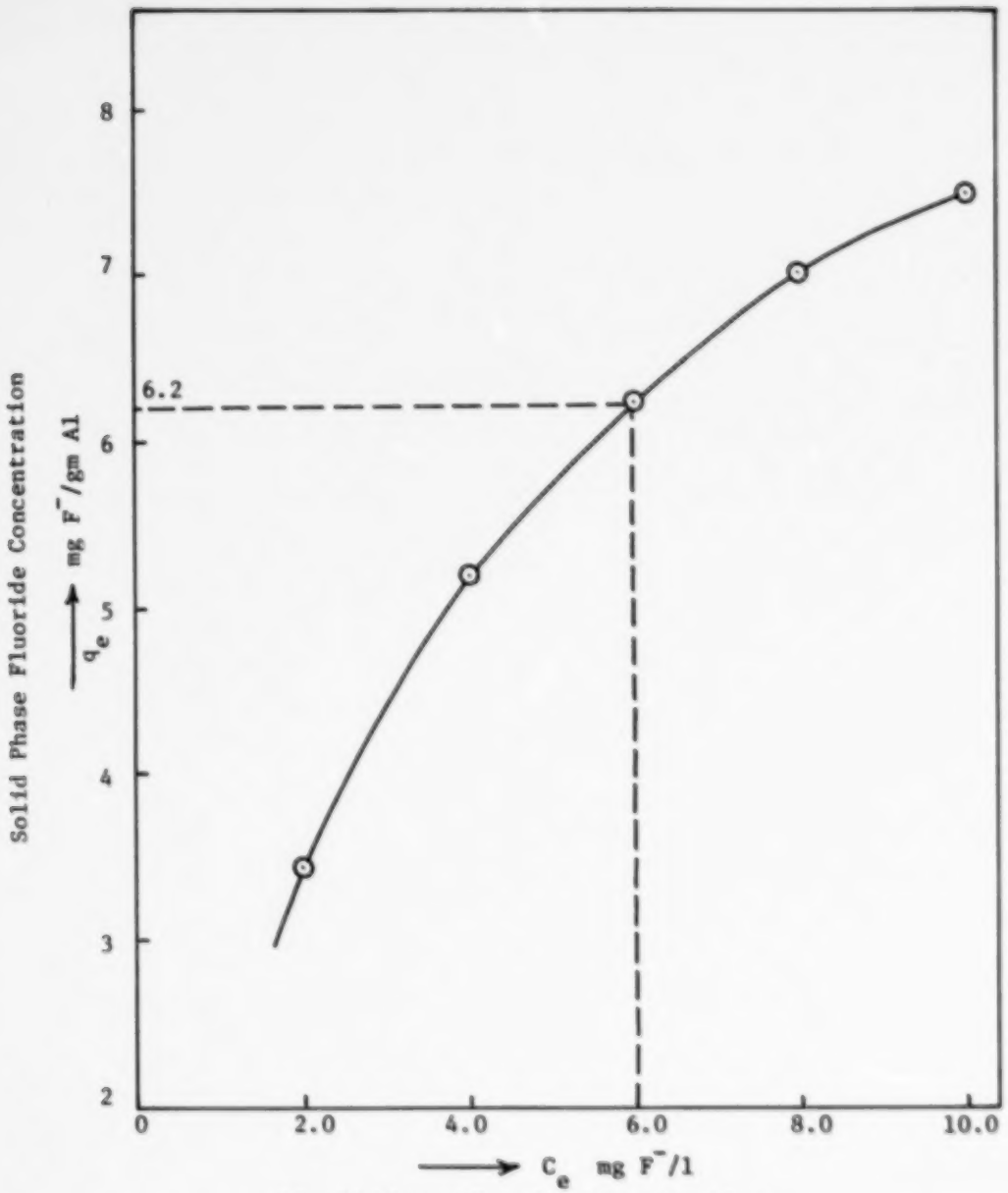


FIGURE 5. FLUORIDE ADSORPTION ISOTHERM

Adsorbate pH = 7.3, temperature = 22°C

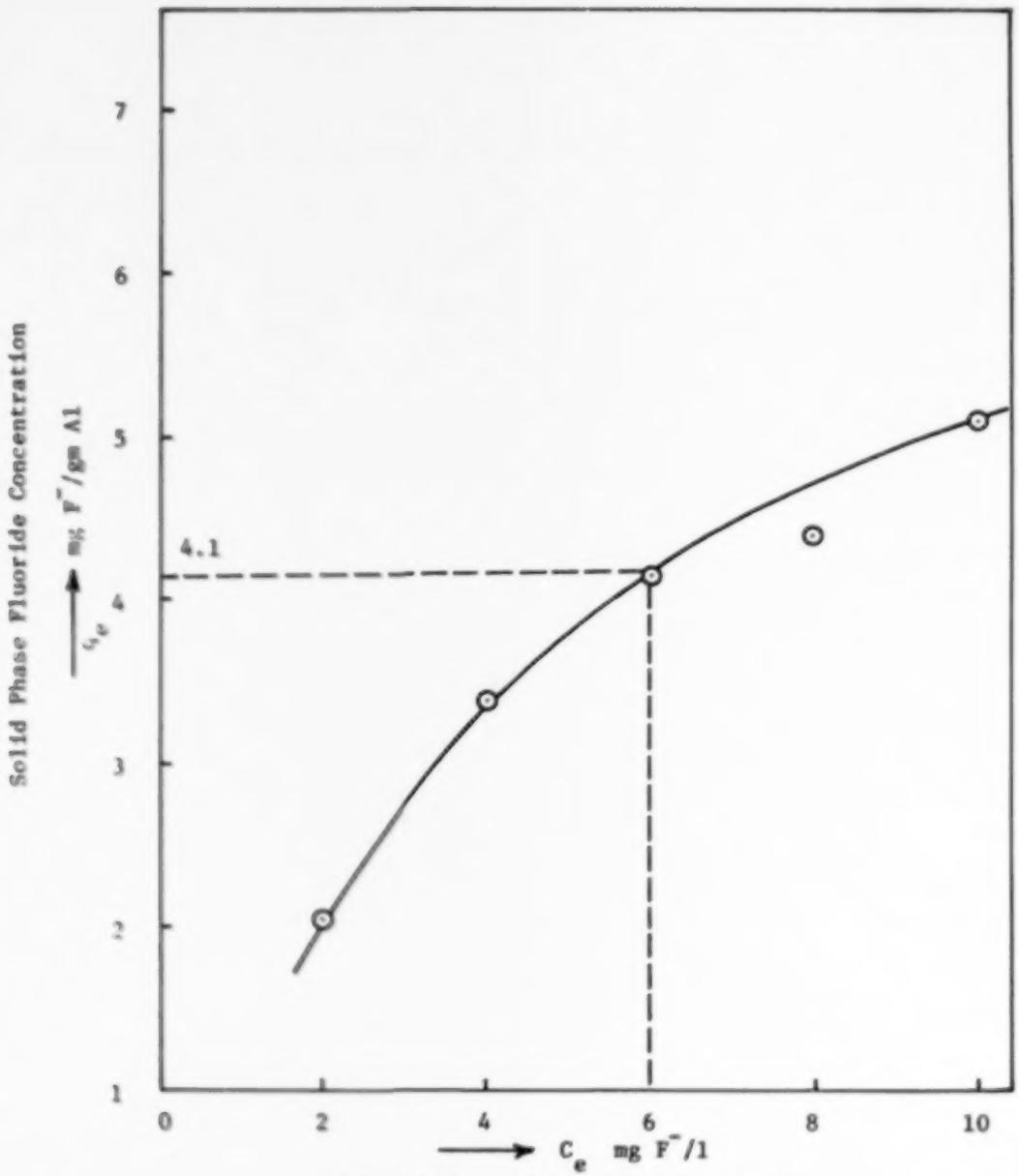


FIGURE 6. FLUORIDE ADSORPTION ISOTHERM

Adsorbate pH = 8.0, temperature = 22°C

fluoride adsorption capacity on activated alumina obtained from these experiments was 10.2 mg/g at pH 5 and pH 6, five times greater than what has been reported in the literature [Savinelli and Black, 1958] but in general agreement with the results of Choi and Chen [1979] for essentially pure fluoride solutions.

EFFECTS OF pH

The effects of pH on the adsorption of fluoride by activated alumina are shown in Fig. 7. For a fixed fluoride concentration, adsorption remains almost constant within the pH range 5.0 to 6.0 after which the adsorption falls steeply until pH 7.5, then continues to decline more gradually as pH is increased.

Experiments could be conducted only between pH 5 and 8. Below pH 5, alumina dissolves to form aluminum complexes such as AlF^{2+}, AlF_2^+, AlF_3, and AlF_4^- (pK 6.16, 5.05, 3.91, and 2.71, respectively). Hence, below pH 5, the column would never reach equilibrium until all the adsorbent dissolved to form ligand compounds. On the other hand, above pH 8, predominant hydroxyl ions are preferred over any other ions for adsorption onto alumina beds.

At pH 5 to 6, in the relative absence of hydroxyl and other competing anions, conditions were most favorable for fluoride to occupy adsorption sites. Equilibrium adsorption at pH 5 and 6 has been found to be 9.9 and 10.3 mg F^-/g Al, respectively, for adsorbate concentration of 6 mg F^-/l.

As the pH was increased above 7, the hydroxyl anions, though present only in small quantity (10^{-7} moles/l), competed for adsorption sites and considerably reduced the adsorption capacity of alumina at equilibrium by 30 percent.

EFFECTS OF SO_4^{2-} IONS

Though sulfate (SO_4^{2-}) ions have been found to be less preferred than fluoride ions in competition for adsorption sites, the presence of sulfate had a pronounced effect upon fluoride adsorption, as reported in Fig. 8. As the sulfate ion adsorbate concentration increased from .5 to 15 meq/l, SO_4^{2-} ion adsorption increased from .1 to .3 meq SO_4^{2-}/g Al, while fluoride adsorption was reduced from .46 F^-/g Al to .38 meq F^-/g Al — a reduction of about 17 percent. By comparison, it should be noted with respect to the removal of fluoride from municipal water supplies that where fluoride contaminant levels are found in excess, SO_4^{2-} ion concentration generally ranges around 250 mg/l or 5.2 meq/l. Extrapolating from the above data, fluoride adsorption under normal circumstances could be reduced by up to 26 percent.

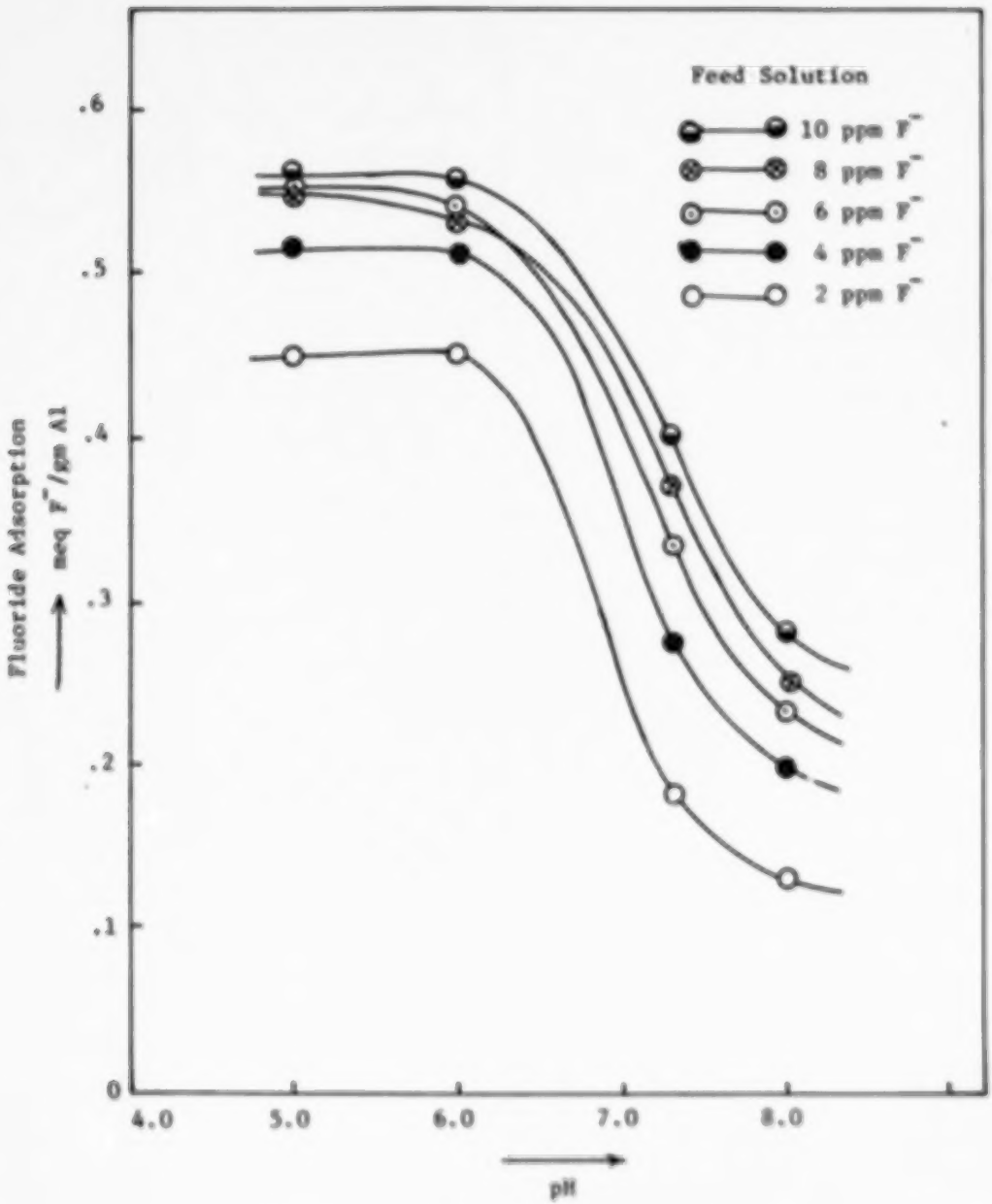


FIGURE 7. pH EFFECT ON FLUORIDE ADSORPTION

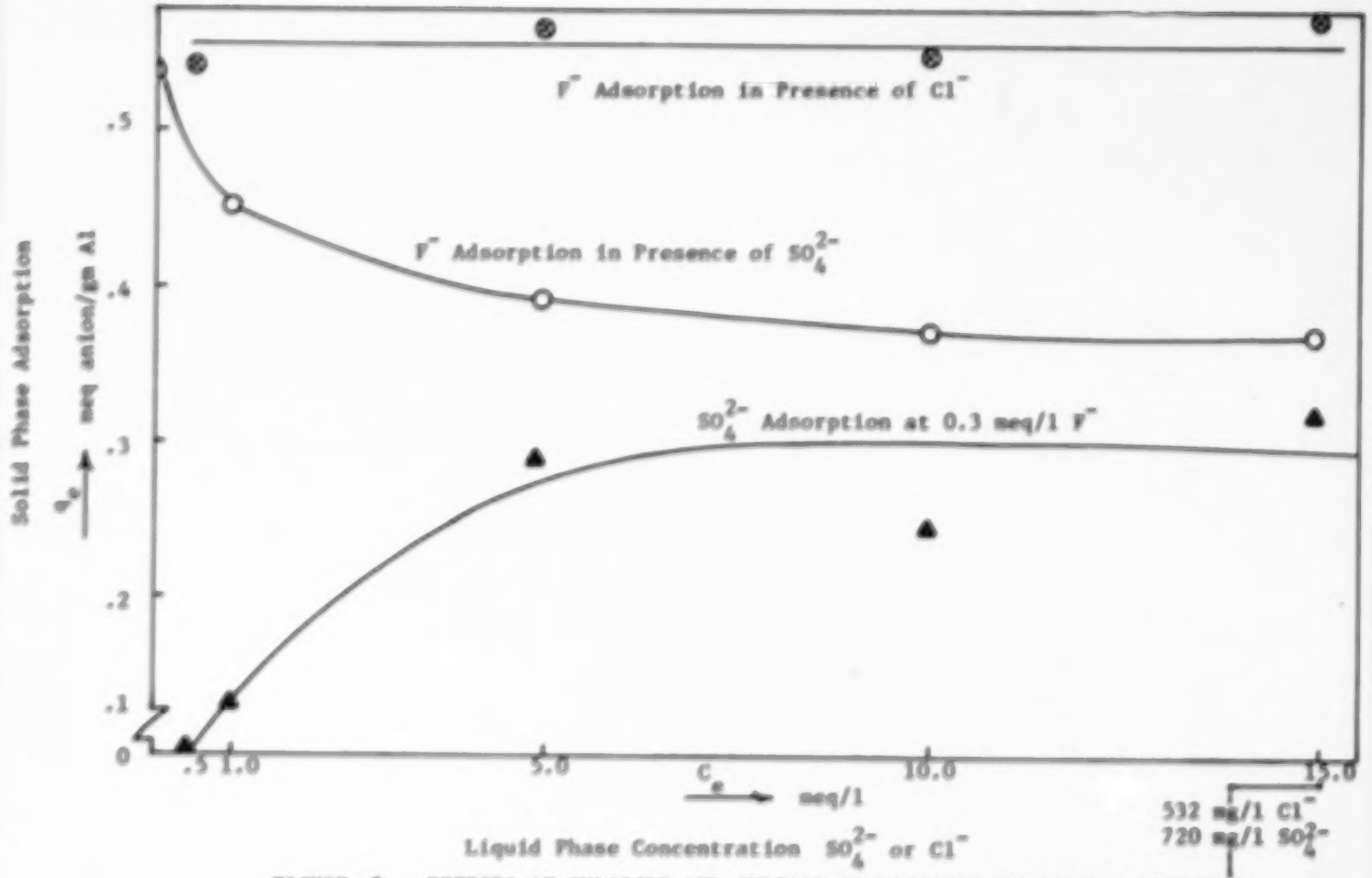


FIGURE 8. EFFECTS OF CHLORIDE AND SULFATE ON FLUORIDE ADSORPTION ISOTHERMS

Adsorbate pH = 6.0, F⁻ Conc. = .3 meq/1 (5.7 mg F⁻/1)

CHLORIDE EFFECTS

The effects of the presence of chlorides (.5 meq/1 to 15 meq/1) on fluoride adsorption was also tested, and the results are depicted in Fig. 8. The adsorbate acidity was fixed at pH 6 and fluoride concentration was kept constant at .3 meq/1 throughout the experiment. As expected, no significant change in fluoride adsorption was observed, demonstrating that the fluoride ion is far more preferred for adsorption by alumina than chloride ions. Thi result was predicted by Umland, whose preferential series presumed chloride to be much less preferred than fluoride which in turn was only slightly less preferred than hydroxide and phosphate for anion adsorption.

A comparison of Figs. 9 and 10 reveals that, whereas variation in SO_4^{2-} concentration affected the fluoride adsorption kinetics to a noticeable extent, variation in chloride concentration did not. This is contrary to the results of Choi and Chen [1979].

Referring to Table 6, it should be noted that although chloride adsorption remained relatively constant with increasing chloride concentration, the amount of fluoride adsorbed slightly increased so that the sum of anionic species adsorbed onto alumina increased with increasing anionic concentration. Furthermore, the total anionic adsorption of the sulfate plus fluoride solution was almost the same as that of chloride plus fluoride solution, suggesting that increasing the concentration of a much less preferred ion might increase the adsorption of the more preferred ion. However, this effect needs to be researched in greater detail.

HIGH IONIC STRENGTH EFFECTS

Fluoride contaminated groundwater found in nature tends to contain levels of dissolved solids, consisting of a variety of cations and anions. The anions are mostly sulfate, chloride, bicarbonates (or carbonates), and nitrate. Another set of experiments was conducted to determine the effect of high ionic strength adsorbate solution on fluoride removal by activated alumina adsorption. Adsorbate solutions were prepared in deionized water with equivalents of sulfate, chloride, and bicarbonate anions. The sum of chloride, sulfate, and bicarbonate concentration ($\Sigma\ Cl^- + SO_4^{2-} + HCO_3^-$) was kept at 3, 6, 12, 24, or 48 meq/1. The ionic strengths of these solutions were 4.0, 8.5, 14.5, 22.5, or 56.5 mmoles/1.

The effect of ionic strength on fluoride adsorption is reported in Figs. 11, 12 & 13. Fluoride adsorption decreased with increasing ionic strength. An analysis of species adsorbed onto the alumina indicated that the reduction in fluoride adsorption was caused by the SO_4^{2-} ion species, while chloride and bicarbonate had an insignificant effect.

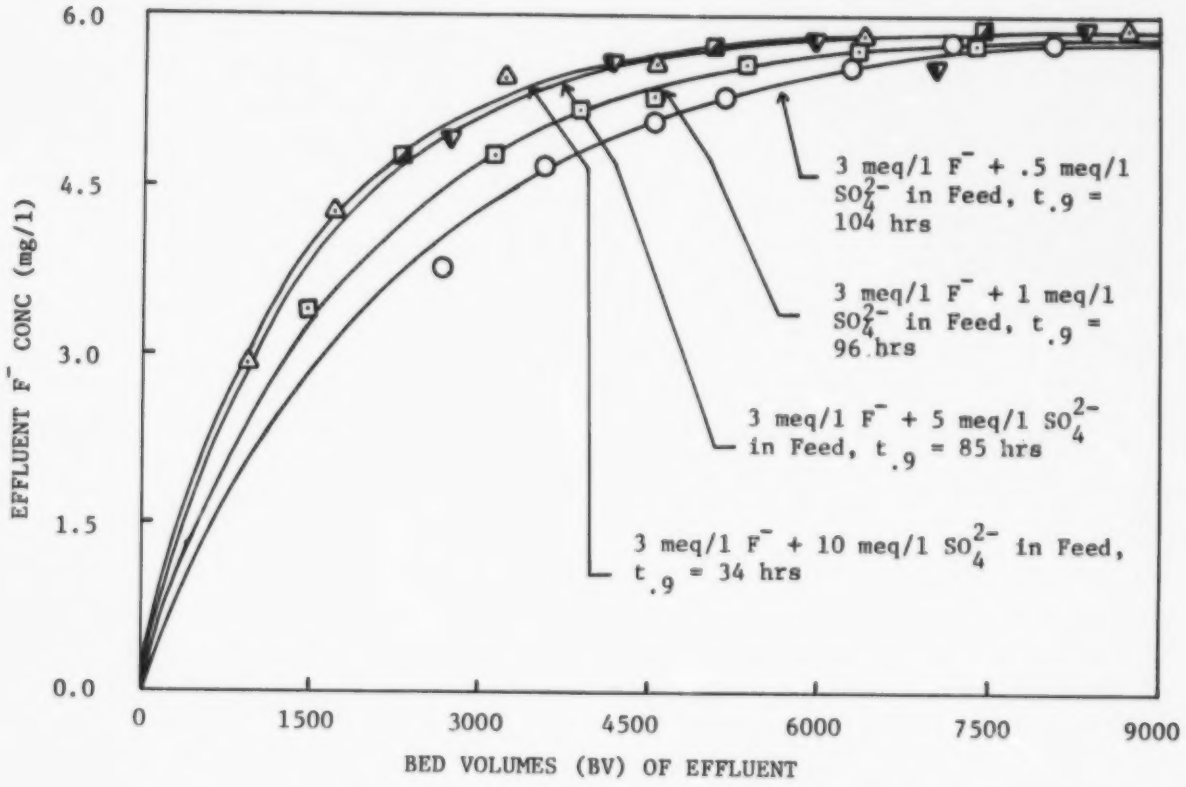

6.0
4.5
3.0
1.5
0.0
EFFLUENT F⁻ CONC (mg/1)
0
1500
3000
4500
6000
7500
9000
BED VOLUMES (BV) OF EFFLUENT
3 meq/1 F⁻ + .5 meq/1 SO4 2- in Feed, t.9 = 104 hrs
3 meq/1 F⁻ + 1 meq/1 SO4 2- in Feed, t.9 = 96 hrs
3 meq/1 F⁻ + 5 meq/1 SO4 2- in Feed, t.9 = 85 hrs
3 meq/1 F⁻ + 10 meq/1 SO4 2- in Feed, t.9 = 34 hrs

FIGURE 9. MINI-COLUMN EFFLUENT CONCENTRATION HISTORIES, pH = 6.0
EFFECT OF SO_4^{2-} CONCENTRATION ON COLUMN KINETICS
Q = 1.1 ml/min, EBCT = .88 min, BV = 1.0 ml
$t_{.9}$ = time to 90% of equilibrium in hours

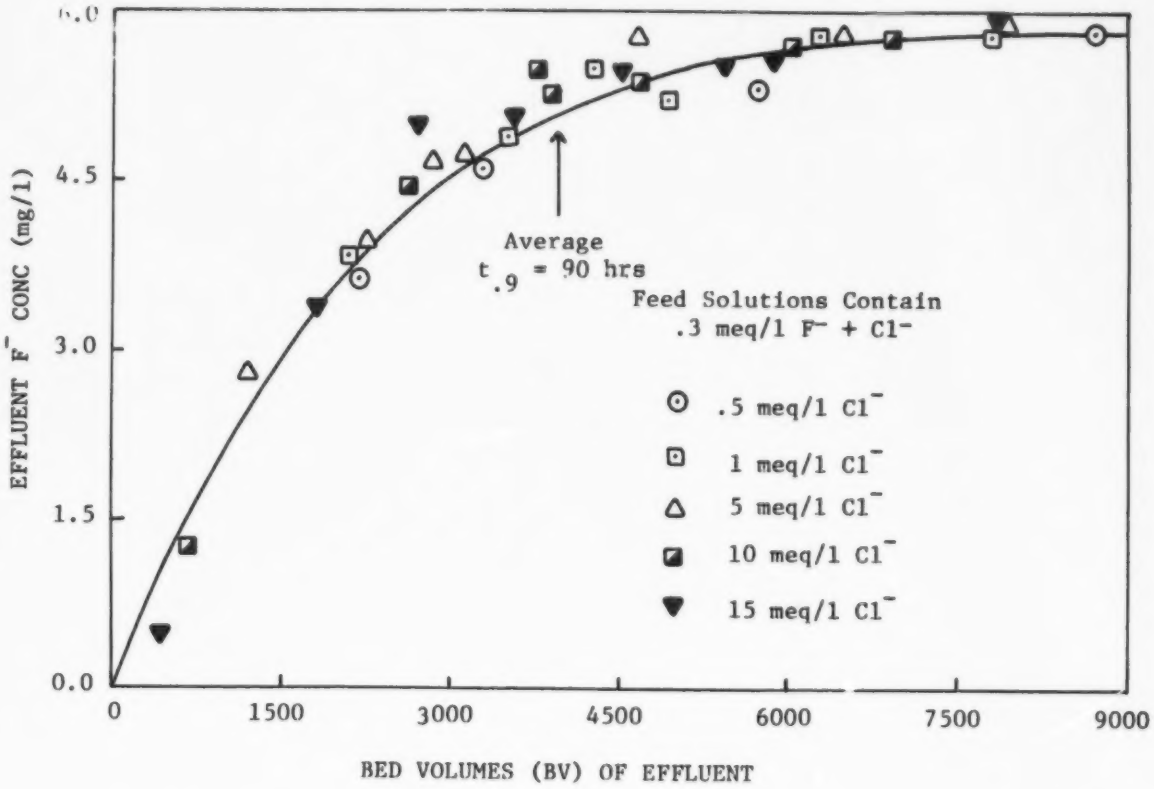


FIGURE 10. MINI-COLUMN EFFLUENT CONCENTRATION HISTORIES, pH = 6.0
EFFECT OF Cl^- CONCENTRATION ON COLUMN KINETICS
Q = 0.78 ml/min, EBCT = 1.2 min, BV = 1.0 ml
$t_{.9}$ = time to 90% of equilibrium in hours

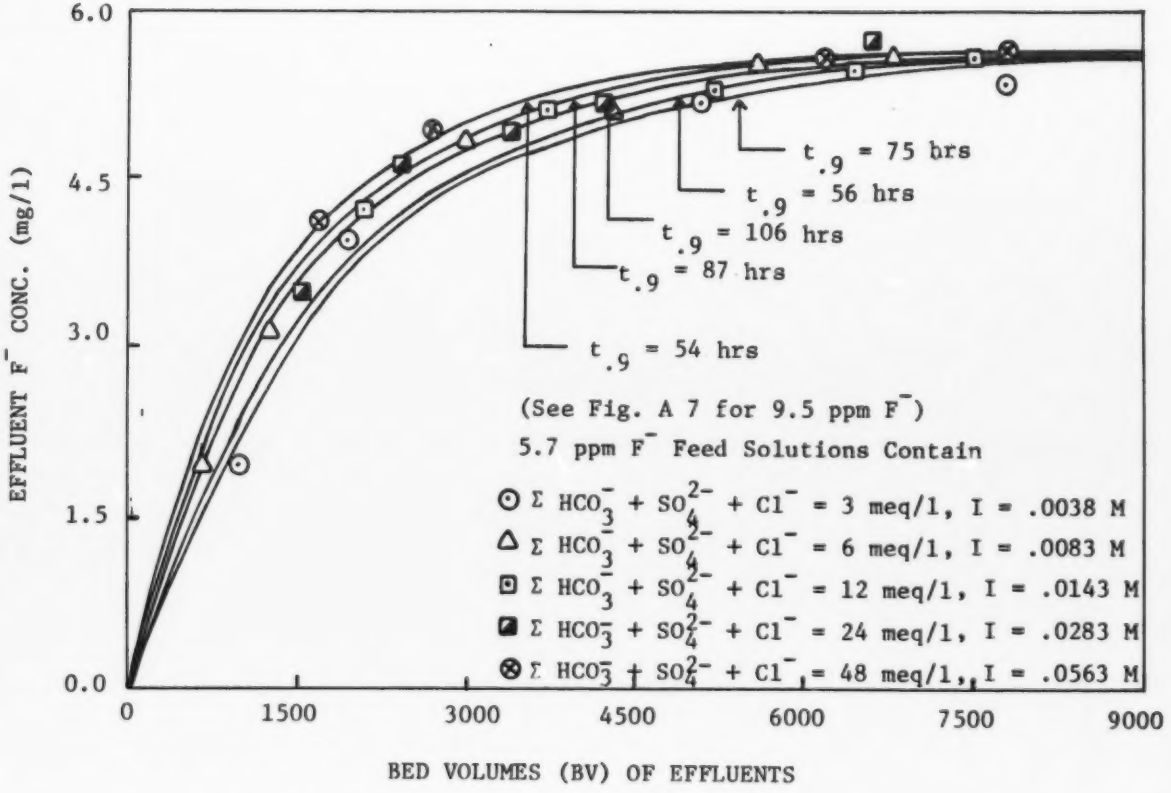

6.0
4.5
3.0
1.5
0.0
EFFLUENT F⁻ CONC. (mg/l)
0
1500
3000
4500
6000
7500
9000
BED VOLUMES (BV) OF EFFLUENTS
t.9 = 75 hrs
t.9 = 56 hrs
t.9 = 106 hrs
t.9 = 87 hrs
t.9 = 54 hrs
(See Fig. A 7 for 9.5 ppm F⁻)
5.7 ppm F⁻ Feed Solutions Contain
⊙ Σ HCO3⁻ + SO4²⁻ + Cl⁻ = 3 meq/1, I = .0038 M
△ Σ HCO3⁻ + SO4²⁻ + Cl⁻ = 6 meq/1, I = .0083 M
⊡ Σ HCO3⁻ + SO4²⁻ + Cl⁻ = 12 meq/1, I = .0143 M
◪ Σ HCO3⁻ + SO4²⁻ + Cl⁻ = 24 meq/1, I = .0283 M
⊗ Σ HCO3⁻ + SO4²⁻ + Cl⁻ = 48 meq/1, I = .0563 M

FIGURE 11. MINI-COLUMN EFFLUENT CONCENTRATION HISTORIES, pH = 7.1
EFFECT OF IONIC STRENGTH ON COLUMN KINETICS
Q = 1.0 ml/min, EBCT = 1 min, BV = 1.0 ml
$t_{.9}$ = time to 90% of equilibrium in hours
See Fig. A 7 for 9.5 ppm F⁻

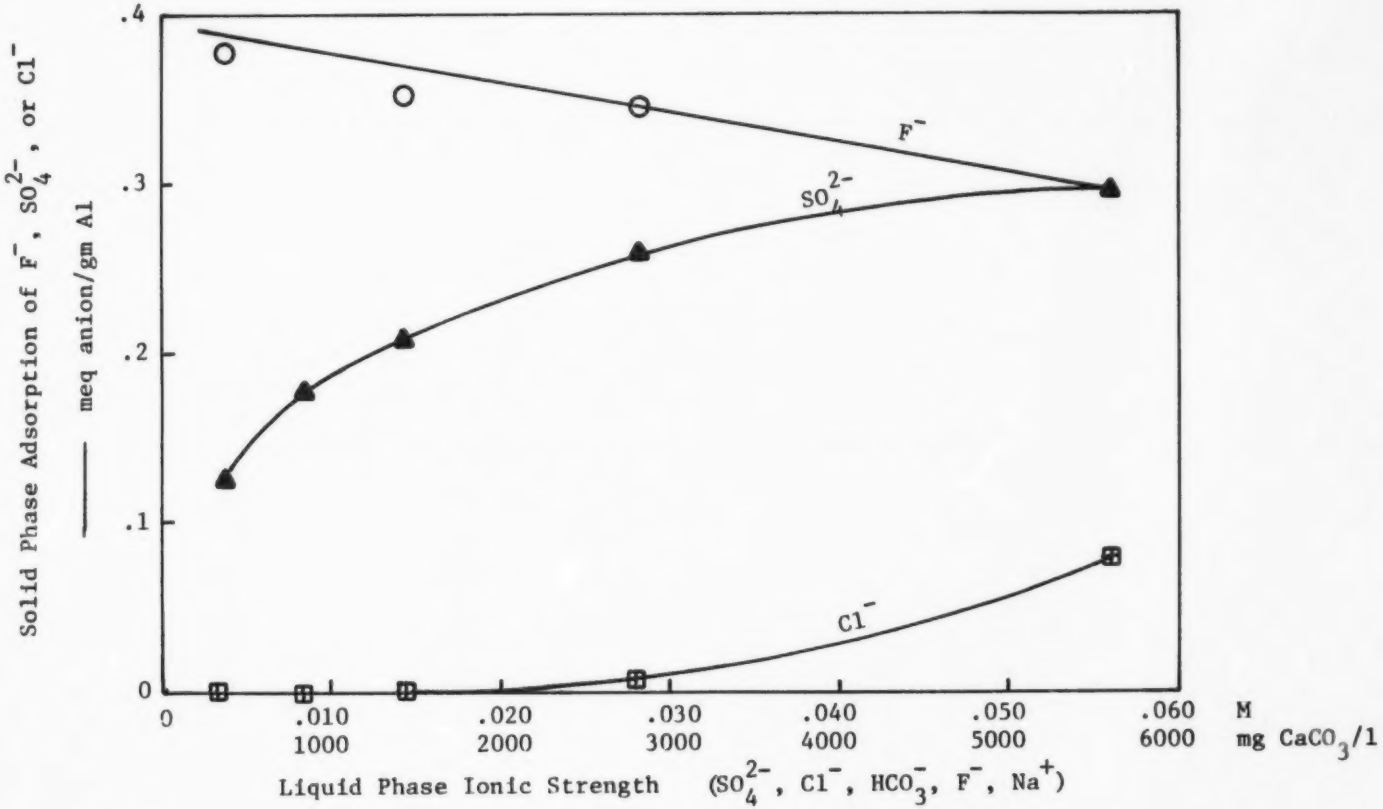


FIGURE 12. ANION ADSORPTION ISOTHERMS

Adsorbate pH = 7.1, F^- strength = .3 meq/1

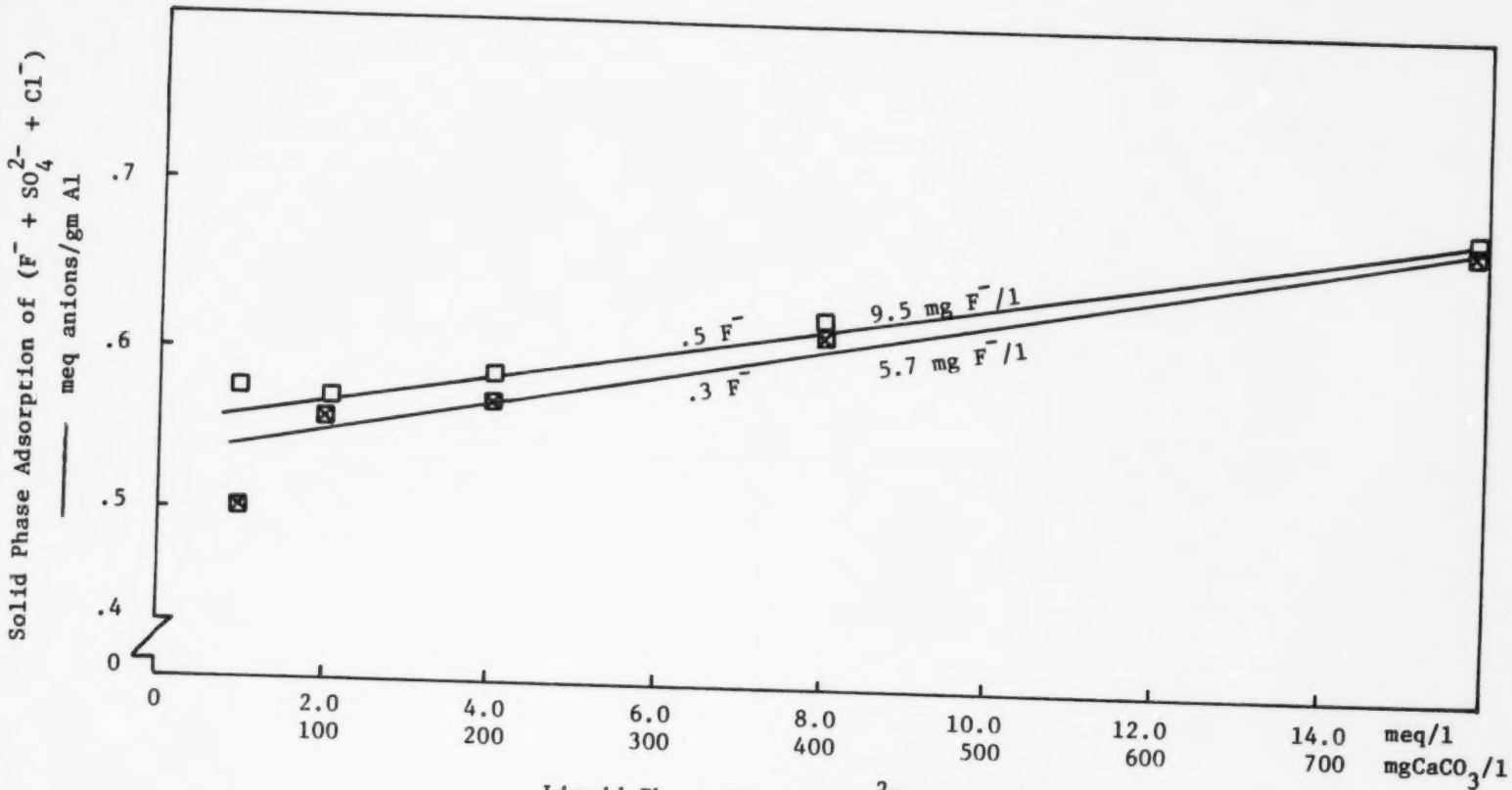


FIGURE 13. ANIONS ADSORPTION ISOTHERM

Adsorbate pH = 7.1, F^- conc. = .3, .5 meq/1

SECTION 6

DISCUSSION

The exact phenomenon by which fluoride is removed from water by activated alumina has yet to be conclusively described. Many authors [Savinelli and Black, 1958] regarded fluoride adsorption as an ion exchange phenomenon while others [Hingston, 1972; Parks, 1967; Muljadi, 1966] considered it typical of adsorption behavior by metal oxides, an aqueous surface phenomenon. However, the information derived from these experiments—concerning the dependence of fluoride adsorption upon initial fluoride concentration, pH, competing anions, and ionic strength—may provide a new foundation for future studies of the kinetics of activated alumina adsorption.

ACTIVATED ALUMINA F^- ADSORPTION CAPACITY

In general, the literature (most notably, Churchill, 1936; Fink and Lindsay, 1936; Swope and Hess, 1937; Zabban, 1967; Maier, 1953) reports much lower capacities of F^- adsorption on activated alumina than were here obtained.

Savinelli and Black, in their bench scale experiments, showed a capacity of 8.8 mg/g Al (3400 grains/cu ft*) at pH 5.6 for C_e = 10 ppm F^-. In recent articles, Yeun C. Wu [1978], and Rubel and Woosley [1979] reportedly attained an optimum adsorption capacity for fluoride on activated alumina of 2620 grains/cu ft Al (6.8 mg/g), and 3200 grain/cu ft Al (8.3 mg/g) respectively. In Rubel and Woosley's pilot scale column experiments, the F^- concentration was 6.0 mg/l and the pH was controlled between 5 and 6. The experiments reported here indicate that, in the absence of competing ions and when acidity is strictly controlled between pH 5.0 and pH 6.0, adsorption capacity can reach as high as 10.1 gm/g Al (3894 grain/ft^3) for an influent F^- concentration of 6 ppm (a high but not uncommon concentration for contaminated underground municipal water supplies). The significantly lower values for the maximum adsorption capacity reported in the early literature may be attributed to a number of factors, such as uncontrolled pH, equilibria obtained from batch reactors, or studies conducted in continuous flow columns which were terminated for practical considerations at some arbitrary fluoride concentration breakthrough and never allowed to reach equilibrium. It is not being suggested here that in field operation, one should always expect these maximum capacities to be achieved. The equilibrium capacities are offered as a goal for ideally efficient processes.

*Note: Above conversions based on packed alumina density of 55 lb/ft^3.

FLUORIDE ADSORPTION ISOTHERMS

The shapes of the isotherms describing fluoride adsorption equilibria were largely determined by such factors as the relative affinity of the solute for the solid surface; the number of sites available for adsorption; and the interactions of the adsorbed molecules. The F^- adsorption isotherms obtained are typical of weak base synthetic resins. They satisfy the Langmuir mathematical model well compared to the Freundlich model; the average correlation coefficients r's are .994 and .971, respectively. Other constants and isotherms are reported in Table 8, and Figs. 14 through 17. In his explanation of the selectivity coefficient for ion exchange, Clifford [1978] reiterated that the Donan membrane equilibrium theory, the law of mass action, and the Langmuir isotherm assumptions all yield the same equilibria expressions. For binary isotherms. the Langmuir multicomponent equilibria theory yields a separation factor constant, α_A^B, such that

$$q_A = \frac{Q' b_A C_A}{1 + b_A C_A + b_B C_B}$$

$$q_B = \frac{Q' b_B C_B}{1 + b_A C_A + b_B C_B}$$

$$\alpha_A^B = \frac{q_B C_A}{q_A C_B}$$

where Q' = Langmuir ultimate solid phase adsorption (or ion exchange) capacity
b_i = Langmuir constant related to adsorption energy

Taking OH^- and F^- ions as the two components, it may be noted that the relative affinity of alumina for OH^- ions is so disproportionately large that the separation factor approaches infinity. As a result, initial acid conditioning and regeneration of the alumina after exhaustion are essential.

EFFLUENT CONCENTRATION HISTORIES (Appendix Figs. A1 - A6)

Further analysis of effluent concentration histories obtained for each mini-column sheds light on several important kinetic relationships.

Considering throughput at 90 percent equilibrium ($T_{.9}$ = meq F^- ions passed/meq F^- capacity on A1) and $t_{.9}$ time for 90 percent exhaustion (both of which are flow rate dependent for a given pH and ionic strength—Tables 5 through 7), $t_{.9}$ is inversely proportional to the influent F^- concentration (Fig. 18) while $T_{.9}$ throughput is directly proportional to the rate of loading. Since a slower flow rate maximizes adsorption, while the practial limitations of treatment plants (such as reactor size and effluent demand) press for a faster flow, a compromise must be accomplished based upon the rate of adsorption, which requires a detailed knowledge of kinetics. Nevertheless, these experimental results do suggest that the kinetics of fluoride

TABLE 8. FLUORIDE ADSORPTION ISOTHERM DATA AT 22°C

pH	C_e mgF⁻/l	q_e mgF⁻/g Al	Other Anions SO_4^{2-} meq/l	Other Anions HCO_3^- meq/l	Langmuir Constants Q' mg/g	Langmuir Constants b_1 1/mg	Langmuir Correlation r	Freundlich Constants K mg/g	Freundlich Constants n g/l	Freundlich Correlation r
5	2	8.39	.005	-	11.62	1.320	.9867	7.778	6.683	.943
	4	9.85	.005	-						
	6	10.62	.006	-						
	8	10.45	.006	-						
	10	10.67	.007	-						
6	2	8.45	.006	-	11.24	1.539	.9899	7.873	7.475	.958
	4	9.77	.006	-						
	6	10.25	.006	-						
	8	10.17	.006	-						
	10	10.60	.006	-						
7	2	3.44	2.500	1.0	10.71	0.236	.9999	2.527	2.037	.994
	4	5.20	2.438	1.0						
	6	6.25	2.500	1.0						
	8	7.03	2.500	1.0						
	10	7.54	2.250	1.0						
8	2	2.45	.625	1.0	7.41	0.239	.9995	1.832	2.122	.992
	4	3.72	,625	1.0						
	6	4.35	.500	1.0						
	8	4.82	.687	1.0						
	10	5.82	.812	1.0						

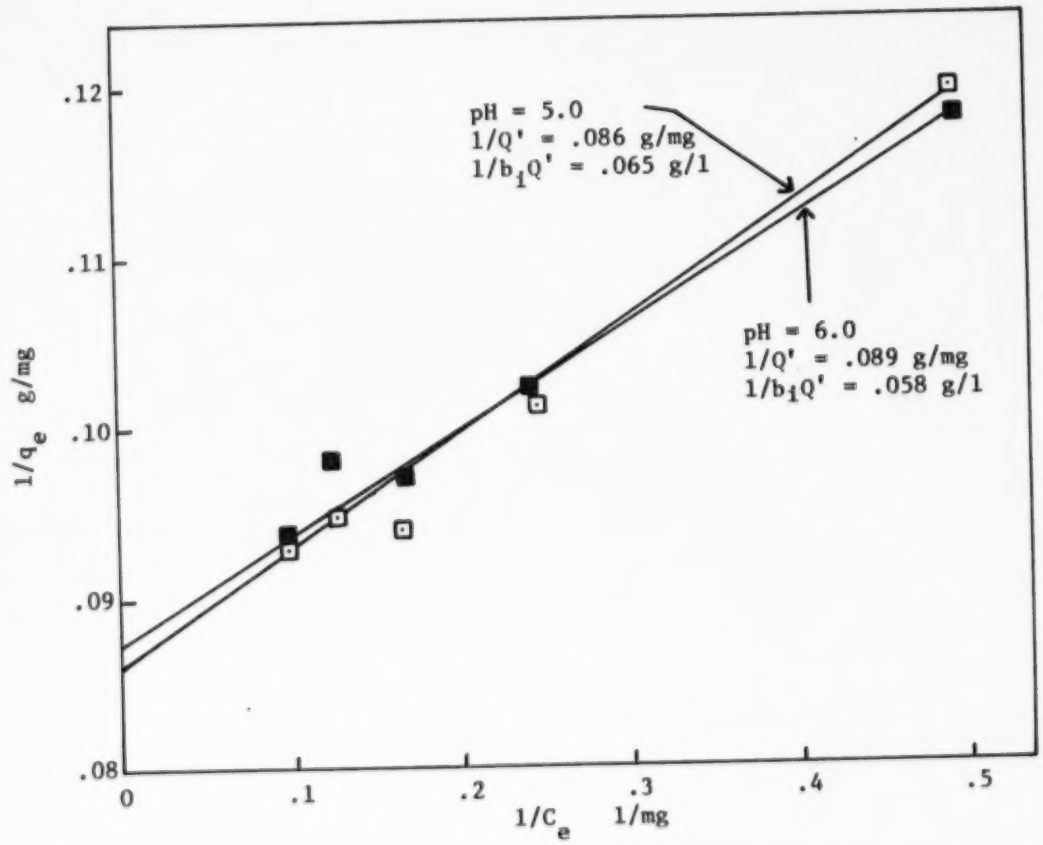


FIGURE 14. LANGMUIR ISOTHERM FOR pH 5, pH 6

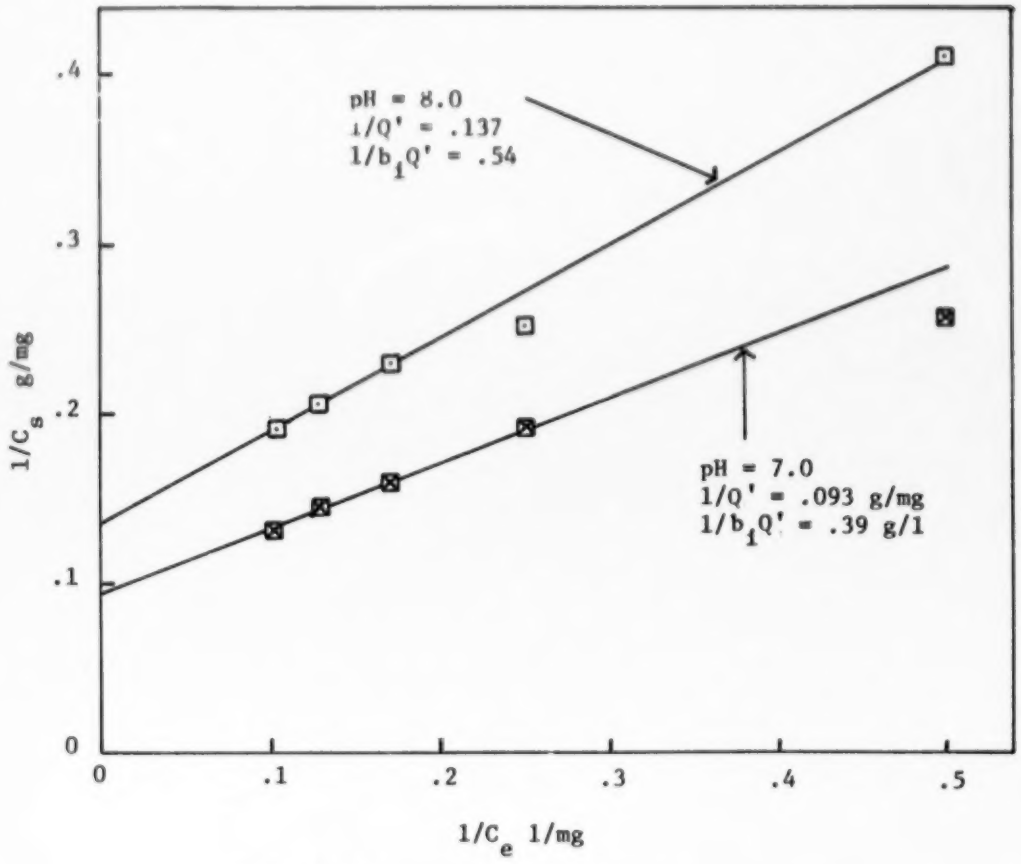


FIGURE 15. LANGMUIR ISOTHERM FOR pH 7, pH 8

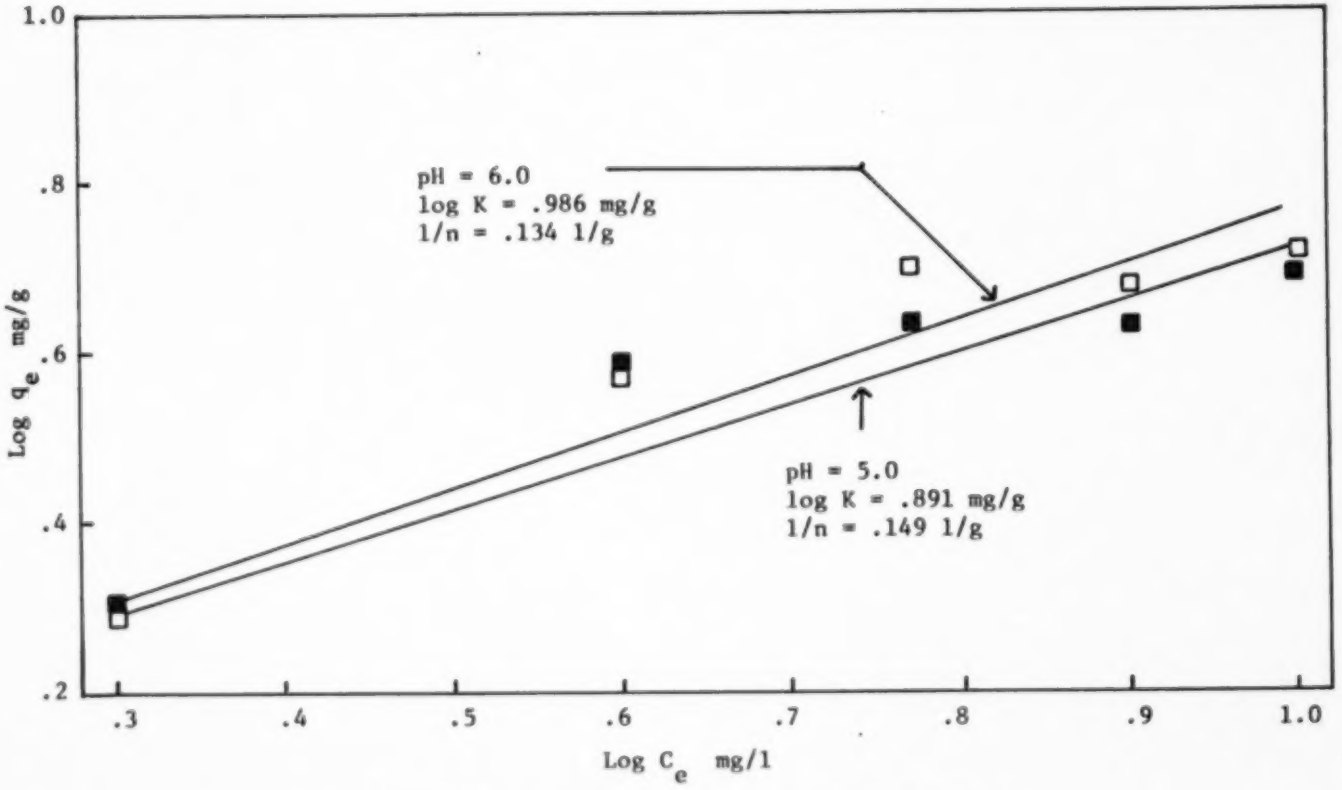


FIGURE 16. FREUNDLICH ISOTHERM FOR pH 5, pH 6

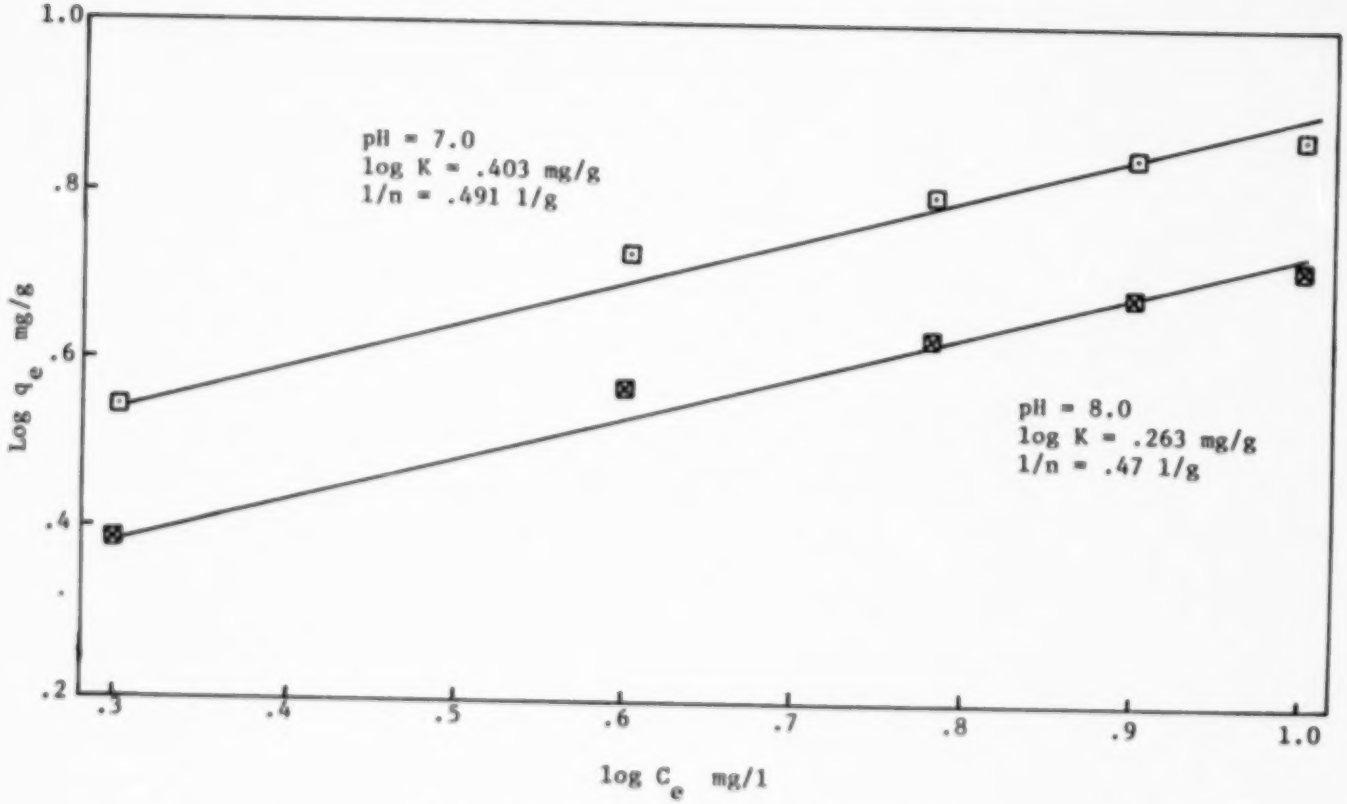


FIGURE 17. FREUNDLICH ISOTHERM FOR pH 7, pH 8

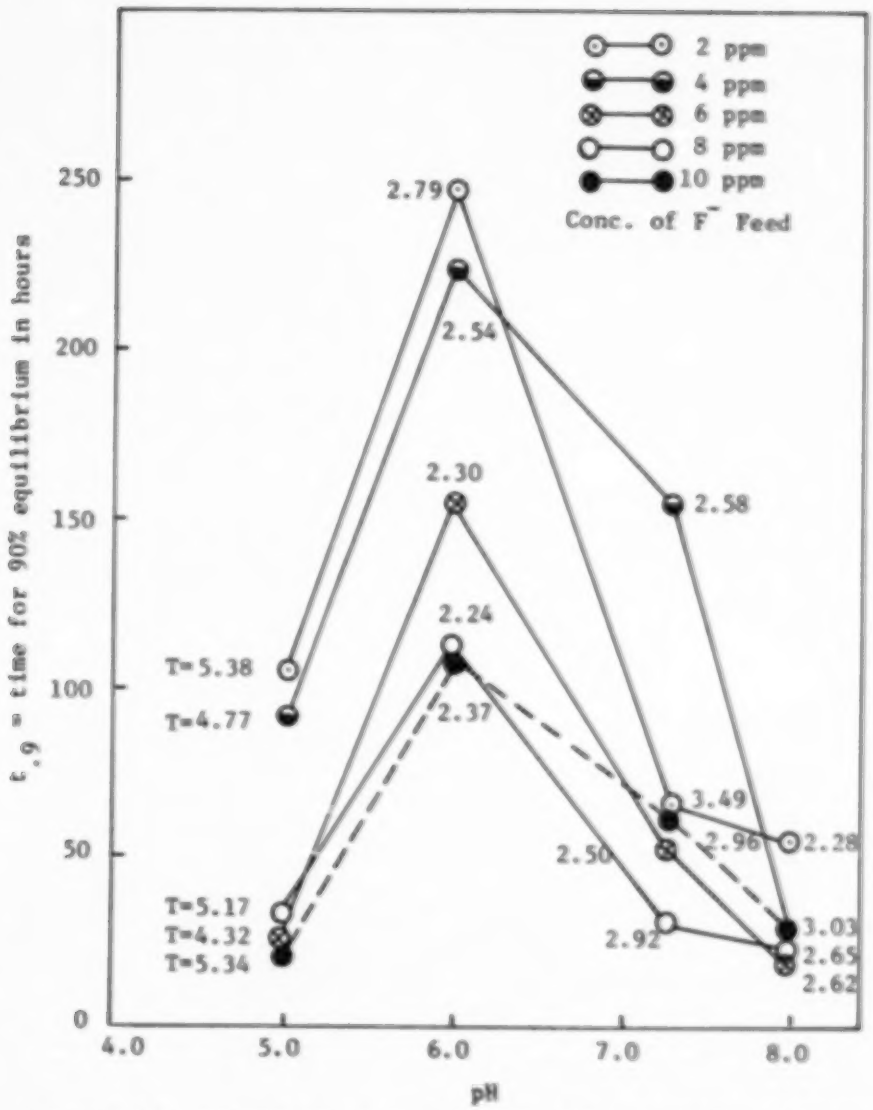


FIGURE 18. EFFECT OF pH ON TIME FOR 90% ADSORPTION EQUILIBRIUM

T = Throughput for given data point
T = number shown adjacent to each point

adsorption on alumina (26 - 48 mesh particles) are very slow—48 hours to reach 50 percent exhaustion of the column and 120 hours to 90 percent exhaustion. Also, in the pH range of 6 - 8, rate of F^- adsorption increases as pH increases.

COMPETING IONS

In concentrations at which they are normally found in drinking water supplies, none of the anions tested (SO_4^{2-}, Cl^-, HCO_3^-) except for OH^- significantly decreased the fluoride adsorption capacity of activated alumina. However, at higher ionic strengths, fluoride adsorption capacity was slightly affected, primarily because of SO_4^{2-} competing ions, indicating that adsorption onto alumina is "fluoride specific." This conclusion is in agreement with the reported preferential sequence of adsorption onto alumina:

$$OH^- \gg F^- \gg SO_4^{2-} \gg Cl^- \gg HCO_3^-$$

The exact values for separation factors between any two anions in the series may be derived after tests for matched pairs of radicals determine the Langmuir mathematical model parameters, i.e., after the binary adsorption isotherms are established.

REFERENCES

1. Activated and Catalytic Alumina, Alcoa Product Data Chemicals, Section GB-2A, Aluminum Company of America, July 14, 1969.

2. Amphlett, C.B. Inorganic Ion exchangers (New York, Elsevier Publishing Company, 1964), p. 90, Fig. 25.

3. Bolt, G.H. and Page, A.L. "Ion Exchange Equations Based on Double Layer Theory," Soil Science, 99, 357 (1965).

4. Choi, Won-Wook and Chen, Kenneth Y., "The Removal of Fluoride from Waters by Adsorption," Journal AWWA, Vol. 71, No. 10, p. 562, October, 1979.

5. Churchill, H.F., U.S. Patent 2,059,552, November 3, 1936.

6. Clifford, Dennis A., "Mobile Pilot-Scale Evaluation of Reverse Osmosis, Ion-Exchange, and Activated Alumina Adsorption for the Treatment of Small Community Water Supplies," A research proposal submitted to US EPA, March, 1978.

7. Clifford, D.A.; Matson, J.V.; Kennedy, Ralph, "Activated Alumina: Rediscovered 'Adsorbent' for Fluoride, Humic Acid, and Silica," Industrial Water Engineering, p. 6, December, 1978.

8. Clifford, D.A., "Nitrate Removal from Water Supplies by Ion Exchange," US EPA-600/2-78-952, June, 1978, p. 34-37.

9. Culp, R.L. and Stoltenberg, H.A., "Fluoride Reduction at LaCrosse, Kansas," J. AWWA, Vol. 50, No. 3, p. 423, March, 1958.

10. Fink, G.J. and Lindsay, F.K., "Activated Alumina for Removing Fluorides from Drinking Water," Ind. and Eng. Chem., Vol. 28, No. 8, p. 947 (1936).

11. Greenwood, D.A., "Some Effects of Inorganic Fluoride on Plants, Animals, and Man," Fifteenth Annual Faculty Research Lecture, The Faculty Association, Utah State Agricultural College, Logan, Utah, 1956, pp. 12-23.

12. Hesse, G. and Sauter, O., "On the Independence of Exchange Adsorption and Van der Waals Adsorption of Aluminum Oxide," Naturwiss., Vol. 34, p. 250 (1947).

13. Hingston, F.J.; Posner, A.M.; and Quirk, J.P., "Anion Adsorption by Geothite and Gilinite: I. The Role of the Portion in Determining Adsorption Envelopes," J. Soil Science, Vol. 23, No. 2, p. 177, June, 1972.

14. Kubli, H.A., "Contribution to the Knowledge of Anion Separation by Means of Adsorption on Alumina," Helv. Chem. Acta, Switzerland, 3:453 (1947).

15. Maier, F.J., "Defluoridation of Municipal Water Supplies," J. AWWA, Vol. 45, August, 1953, p. 879.

16. Muljadi, D.; Posner, A.M.; and Quirk, J.P., "The Mechanism of Phosphate Adsorption by Kaolinite, Gibbsite, and Psuedoboehmite I," J. Soil Science, Vol. 17, p. 212, September (1966).

17. Committee on Biological Effects of Atmospheric Pollutants, Division of Medical Sciences National Research Council, Biological Effects of Atmospheric Pollutants: Fluorides, National Academy of Sciences, Washington, D.C., 1971, pp. 209-214.

18. Parks, G.A., "The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems," Chem. Rev., 65:117 (1965).

19. Rubel, F., Jr. and Woosley, R.D., "The Removal of Excess Fluoride from Drinking Water by Activated Alumina," J. AWWA, 71:1:45 (January, 1979).

20. Savinelli, E.A. and Black, A.P., "Defluoridation of Water with Activated Alumina," J. AWWA 50:1:33 (January, 1958).

21. Schwalb, G.M. and Dattler, G., "Inorganic Chromatography," Agnew. Chemie, Vol. 50, No. 33, p. 691 (August, 1937).

22. Shimkin, M.B.; Arnold, F.A., Jr.; Hawkins, J.W.; and Dean, H.T., "Medical Aspects of Fluorosis," American Association Advancement Sciences, 1953.

23. Sognnaes, R.F., "The Problem of Providing Optimum Fluoride Intake for Prevention of Dental Caries," A Report of the Committee on Dental Health, Publication 294, November, 1953, p. 4.

24. Swope, H.G. and Hess, R.H., "Removal of Fluorides from Natural Waters by Deflurite," Ind. and Eng. Chem., Vol. 29, No. 4, p. 424 (1937).

25. Texas Department of Health, "Community Water Systems in Texas Which Exceed the MCL for Fluroides as Set by the National Interim Primary Drinking Water Regulations, 18 pages, Texas Department of Health, Austin, Texas, March, 1977.

26. Umland, F., "The Interaction of Electrolyte Solutions and α-Al_2O_3: IV: Development of a Formal Ion Exchange Theory for the Adsorption of Electrolytes from Awueous Solutions," Z. Electrochem., V. 60, p. 711 (1956).

27. Federal Register, U.S. EPA, "National Interim Primary Drinking Water Regulations," Washington, D.C., December 24, 1975.

28. U.S. Public Health Service, Drinking Water Standards, 1962.

29. Van Olphen, H., An Introduction to Clay Colloid Chemistry, Interscience, New York, 1963.

30. World Health Organization, "Toxic Effects of Larger Doses of Fluoride," Fluorides and Human Health, WHO Monograph Series No. 59, Geneva: WHO, 1970, pp. 238-239.

31. Zabban, Walter and Jewett, N.W., "The Treatment of Fluoride Wastes," Proc. 22nd Ann. Purdue Industrial Waste Conference, Engrs. Bull. No. 129 (1967).

32. Parks, G.A., "Aqueous Surface Chemistry of Oxides and Complex Oxide Minerals. Equilibrium Concepts in Natural Water Systems," Advances in Chemistry Series, 67, Robert C. Gould (Editor), American Chemical Soceity Publications, Washington, D.C., 1967.

33. Wu, Yeun C., "Activated Alumina Removes Fluoride IOns from Water," Water and Sewage Works, Vol. 125, No. 6, p. 76, June, 1978.

34. Zhabrova, G.M. and Eorov, E.V., "Sorption and Ion Exchange on Amphoteric Oxides and Hydroxides," Russian Chemical Reviews, Vol. 30, No. 6, p. 338, 1961.

APPENDICES

MODIFIED TURBIDIMETRIC METHOD FOR SULFATE DETERMINATION

Reference: Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 344.

1. Place 100 ml sample in 300 ml Erlenmeyer flask.
2. Add 5 ml conditioning reagent.
3. Add one "scoop" (0.2 - 0.3 ml) of reagent-grade barium chloride.
4. Shake by hand, swirling occasionally, for one minute.
5. Allow 4 additional minutes for turbidity to develop with no additional agitation.
6. Set 10 ppm sulfate to read "40" on 0 - 100 scale of Hach turbidimeter (Model 2100A) using 25 ml sample and no spacer in the reading chamber.
7. Read turbidity of all standards and samples after exactly four minutes of turbidity development following initial one minute agitation period.
8. Plot NTU versus ppm sulfate and read off samples.

Notes:
a. Linear range is 2 - 10 ppm sulfate
b. Standard typically, 2, 4, 6, 8, and 10 ppm sulfate
c. See Standard Methods for Preparation of reagents and standards.

FLUORIDE DETERMINATION PROCEDURE WITH ELECTRODES USING 901 IONALYZER

Reference: Orion Analyzer Instruction Manual, Fluoride Electrode Model 96-09.

1. Prepare 10 ppm and 2 ppm standard fluoride solutions from the 100 ppm stock solution.
2. Add 25 ml TISAB II or IV to each 25 ml of above standard and samples to be tested.
3. Set the standard value switch to 10. Set the slope switch to the slope of the electrode, that is, 56.0 mV/decade.
4. Place electrode in 50 ml of 10 ppm standard solution. Press Clear/Read mV and wait for a stable reading. Press Set Concentration. Check the slope by placing electrode in 2 ppm standard solution.
5. Place the electrode in 50 ml of sample solution, wait for a stable reading, and record sample concentration. Similarly repeat step for other samples.

Notes:
a. For every change of standard or sample solution, electrode should be rinsed and fillter dried before placing it in the solution.

b. TISAB II and TISAB IV ionic strength adjustors were prepared as per Orion Ionalyzer Instruction Manual, Fluoride Electrodes Model 94-09, Model 96-09.
c. TISAB IV was used only for testing NaOH-eluted samples because they contained high concentrations of Al.

POTENTIOMETRIC TITRATION METHOD FOR CHLORIDE

Reference: Clifford, Dennis A., "Nitrate Removal from Water Supplies by Ion Exchange," EPA 600/2-78-052, June, 1978, p. 250.

1. Make sample to be titrated up to approximately 50 ml in a 150 ml beaker with teflon-coated magnetic stirring bar.
2. Titrate with .0141 N $AgNO_3$ (.500 meq Cl/ml) to +275 mV end point. This was previously determined to coincide with the inflection point in the ml titrant adder versus mV plot. Potential due to increase in Ag^+ ion was measured using double junction (nitrate-external) calomel, reference electrode (Orion 90-02-00) with Ag/AgS solid state specific ion electrode (Orion 94-10A).

Notes:
a. Sensitivity is 125 mV/ml titrant added at inflection point for .0141 N $AgNO_3$.
b. $AgNO_3$ standardized against 1000 ppm NaCl.

BICARBONATE DETERMINATION WITH TOC ANALYZER

Reference: Beckman Model 95 TOC Analyzer Instruction Manula, for instrument operations.

1. Prepare 10, 20, 40, and 100 ppm $NaHCO_3$ standards from freshly prepared $NaHCO_3$ stock solution.
2. Rinse syringe at least twice by discharging contents elsewhere (not back into beaker). Draw sample up slowly.
3. Inject into inroganic channel of TOC analyzer and set recordings to standardize.
4. Make at least duplicate injections or repeat until reproducible peaks are obtained.
5. Repeat Steps 2, 3, and 4 for all unknown samples and from peak heights calculate HCO_3^- in samples.

TYPICAL CALCULATIONS

For Run No. 34:

$$\alpha_S^F = \frac{\frac{Y_F}{X_F}}{\frac{Y_S}{X_S}} = \frac{Y_F X_S}{X_F Y_S}$$

$$= \frac{[.371][10]}{[.300][.246]} = 50.2$$

TABLE A1

TIME SPENT IN HOURS FOR THROUGHPUT T = 1

Run No.	Hours	Run No.	Hours
1	16.49	26	23.74
2	19.54	27	10.62
3	19.26	28	7.41
4	13.28	29	7.22
5	7.54	30	10.60
6	11.75	31	28.34
7	6.17	32	32.12
8	10.26	33	20.09
9	4.49	34	12.42
10	6.74	35	12.98
11	100.49	36	34.22
12	77.96	37	31.87
13	82.39	38	53.01
14	53.63	39	26.17
15	62.19	40	51.79
16	73.37	41	17.16
17	50.05	42	26.99
18	60.76	43	15.57
19	45.73	44	25.20
20	23.03	45	14.96
21	19.50	46	12.64
22	13.48	47	18.57
23	20.92	48	19.26
24	10.17	49	14.85
25	23.27	50	10.24

TABLE A2 CONVERSION FACTORS

1.00	milliequivalent fluoride	=	19.00 mg fluoride
1.00	gram	=	15.43 grains
1.00	gram alumina	=	1.067 ml alumina (See Note 2) (1.134)
1.00	gram alumina	=	0.00003768 (ft^3 alumina (0.00004005)
1.00	mg F^-/g alumina	=	409.5 g F^-/ft^3 alumina (385.3)
1.00	meq F^-/g alumina	=	7782 grains F^-/ft^3 alumina (7320)
1.00	meq F^-/ml alumina	=	8303 grains F^-/ft^3 alumina

Notes: (1) Alumina is dilute-H_2SO_4-treated Alcoa F-1 grade activated alumina, 26x48 mesh, conditioner according to the procedure given on page 12.

(2) Alumina bulk densities are based on dilute-H_2SO_4-treated, loosely packed, conditioned alumina whose weight was determined after drying for 48 hrs at 110°C. The experimental bulk density of 1.00 g/1.067 ml corresponds to 58.5 lbs/ft^3, i.e., 6.4% higher than the 55 lbs/ft^3 (manufacturer's data) reported for packed alumina in Table 4, p. 13. The values in parentheses are based on 55 lbs/ft^3.

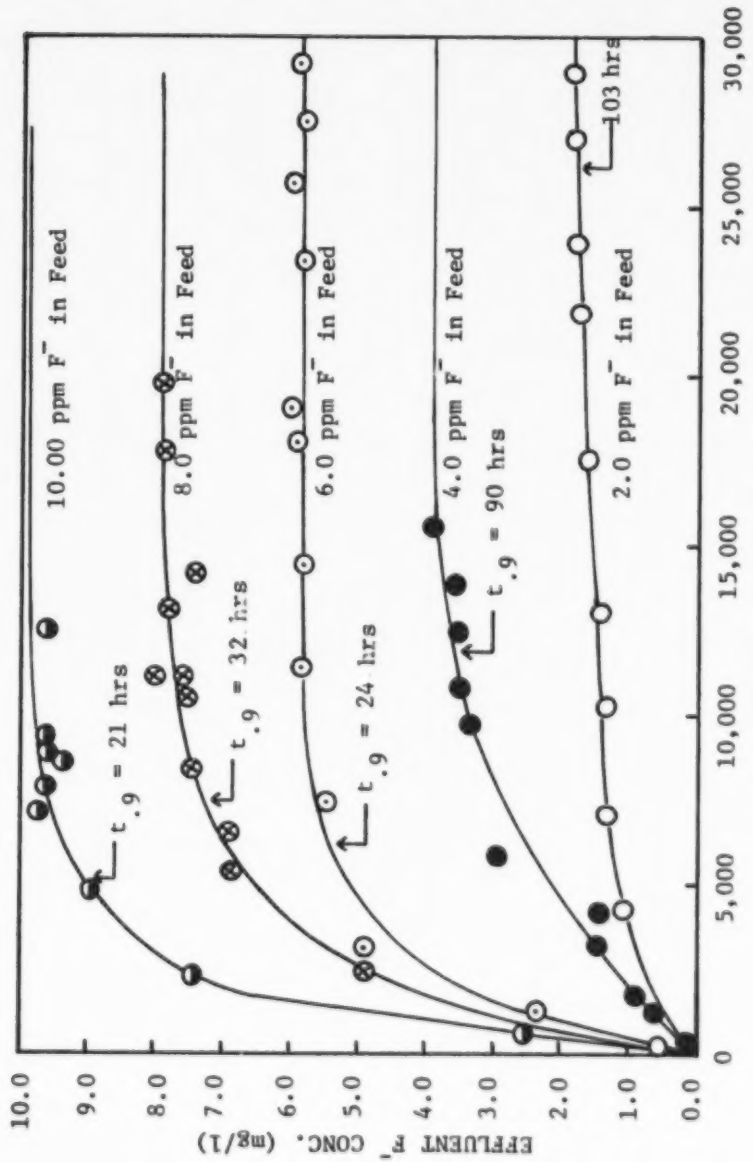


FIGURE A1 MINI-COLUMN EFFLUENT CONCENTRATION HISTORIES, pH = 5.0
EFFECT OF CONCENTRATION ON COLUMN KINETICS
Q = 3.55 ml/min, EBCT = .28 min
BV = 1.0 ml, $t_{.9}$ = time to 90% of equilibrium in hours

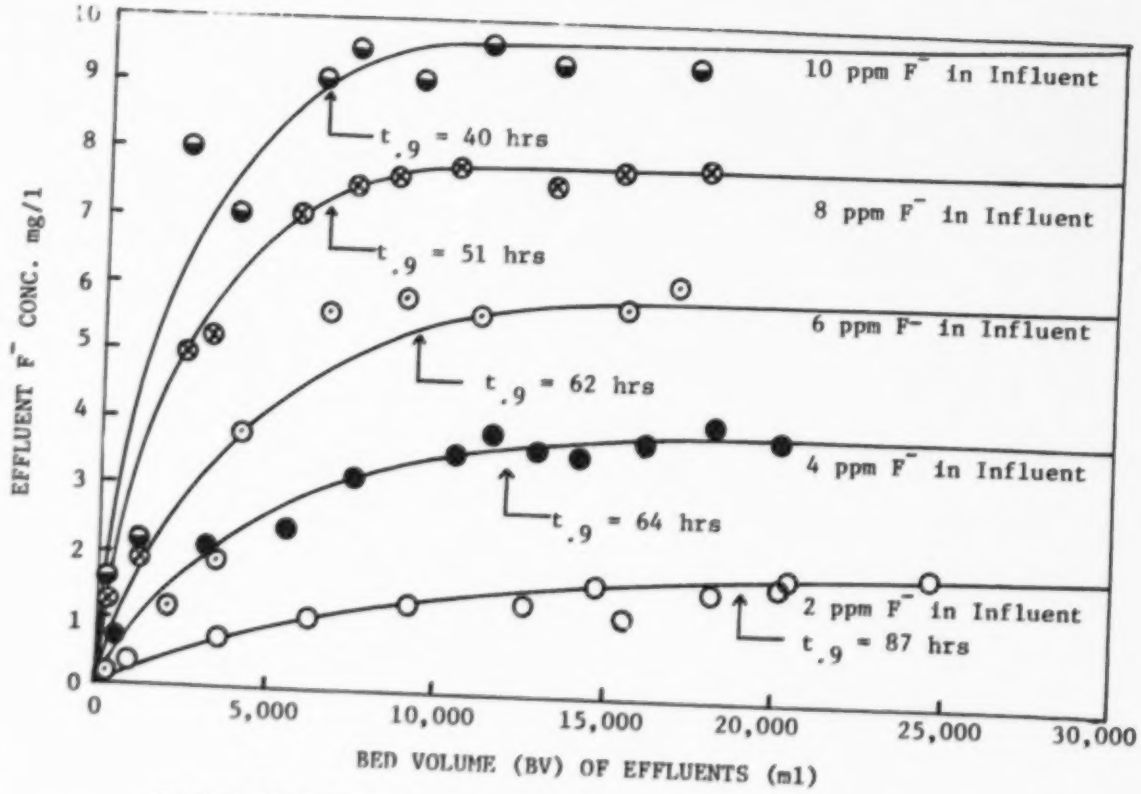


FIGURE A2 MINI-COLUMN EFFLUENT CONCENTRATION HISTORIES, pH = 5.0
EFFECT OF CONCENTRATION ON COLUMN KINETICS
Q = 2.79 ml/min, EBCT = .35 min, BV = 1.0 ml
$t_{.9}$ = time to 90% of equilibrium in hours

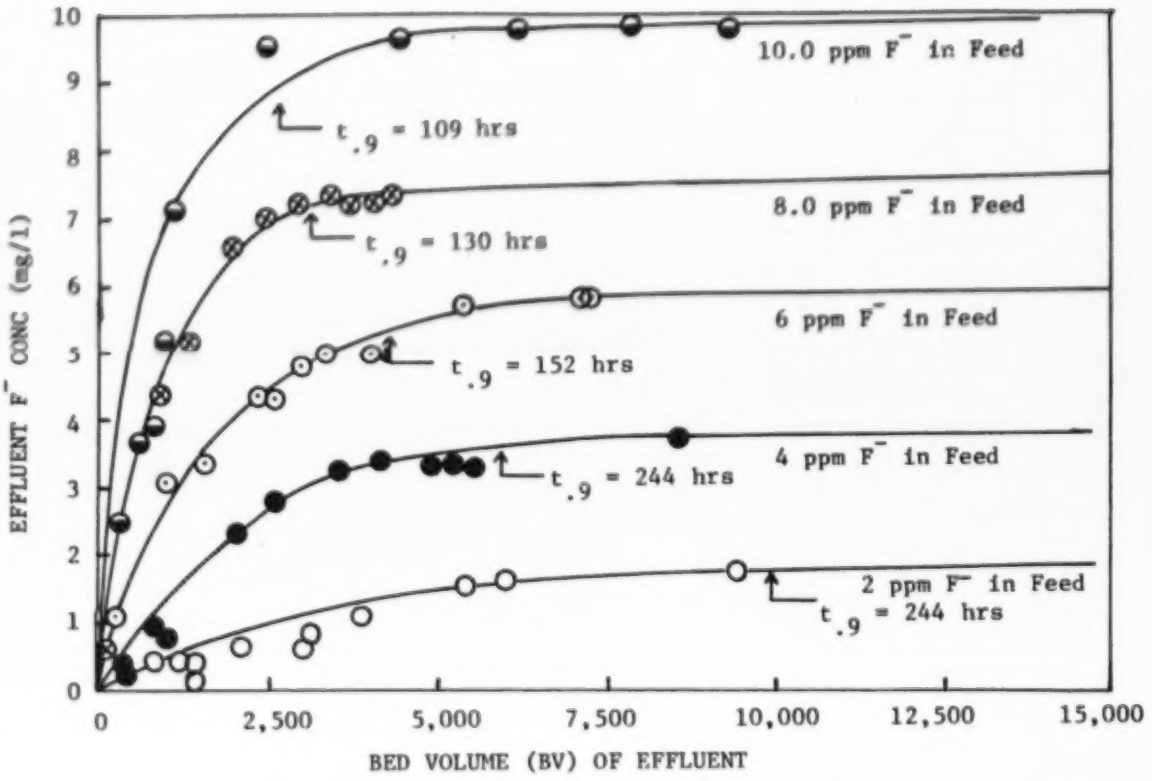


FIGURE A3 MINI-COLUMN EFFLUENT CONCENTRATION HISTORIES, pH = 6.0
EFFECT OF CONCENTRATION ON COLUMN KINETICS
Q = 0.5 ml/min, ETCT = 2 min, BV = 1.0 ml
$t_{.9}$ = time to 90% of equilibrium in hours

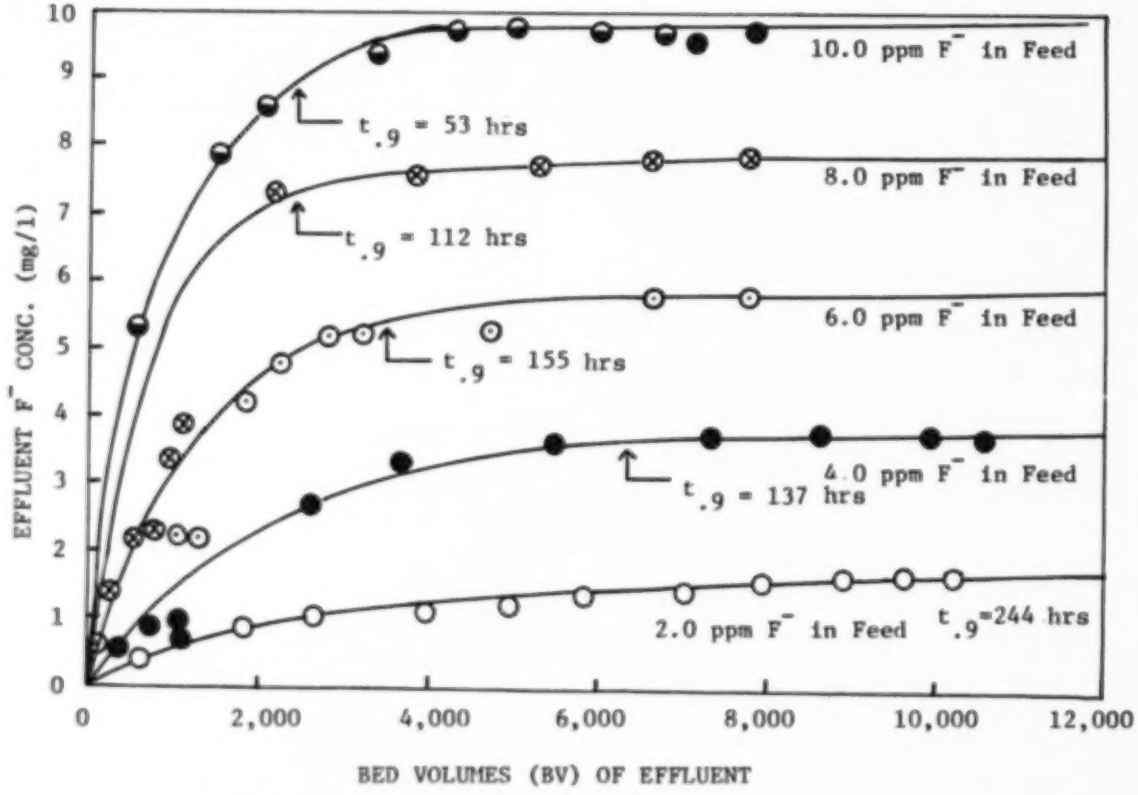


FIGURE A4 MINI-COLUMN EFFLUENT CONCENTRATION HISTORIES, pH = 6.0
EFFECT OF CONCENTRATION ON COLUMN KINETICS
Q = 0.5 ml/min, EBCT = 2 min, BV = 1.0 ml
$t_{.9}$ = time to 90% of equilibrium in hours

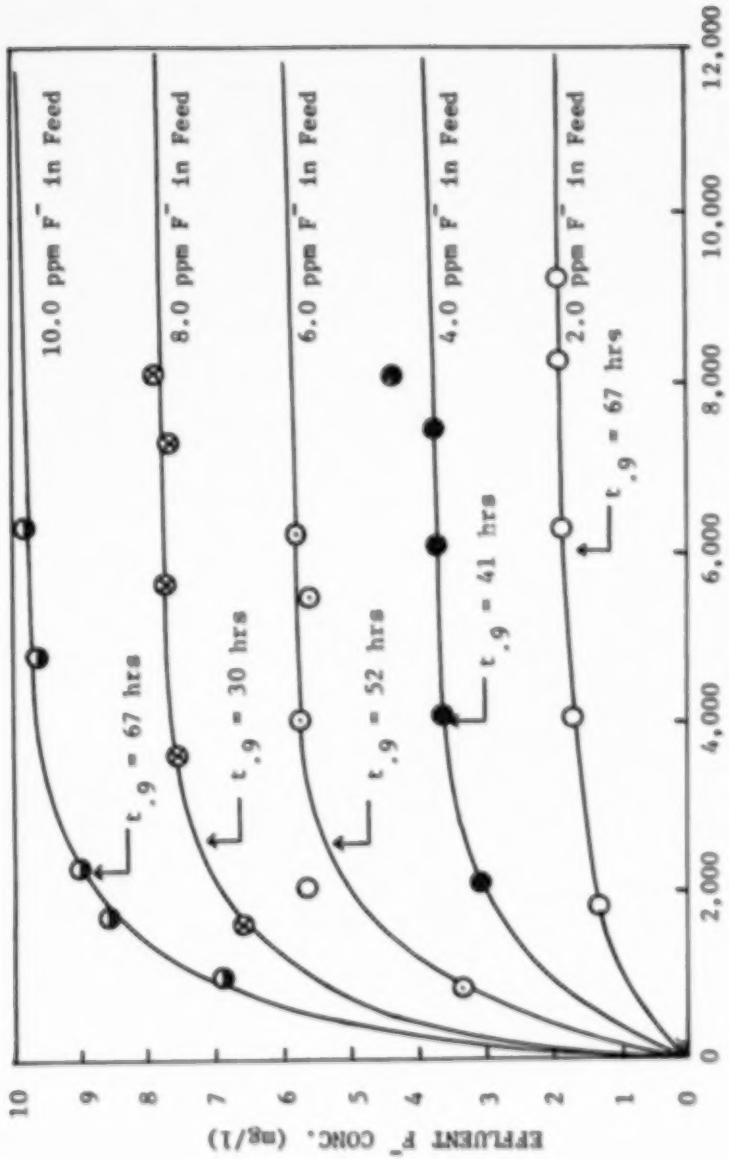


FIGURE A5 MINI-COLUMN EFFLUENT CONCENTRATION HISTORIES, pH = 7.0
EFFECT OF CONCENTRATION ON COLUMN KINETICS
Q = 1.78 ml/min, EBCT = .84 min, BV = 1.0 ml
t .9 = time to 90% of equilibrium in hours

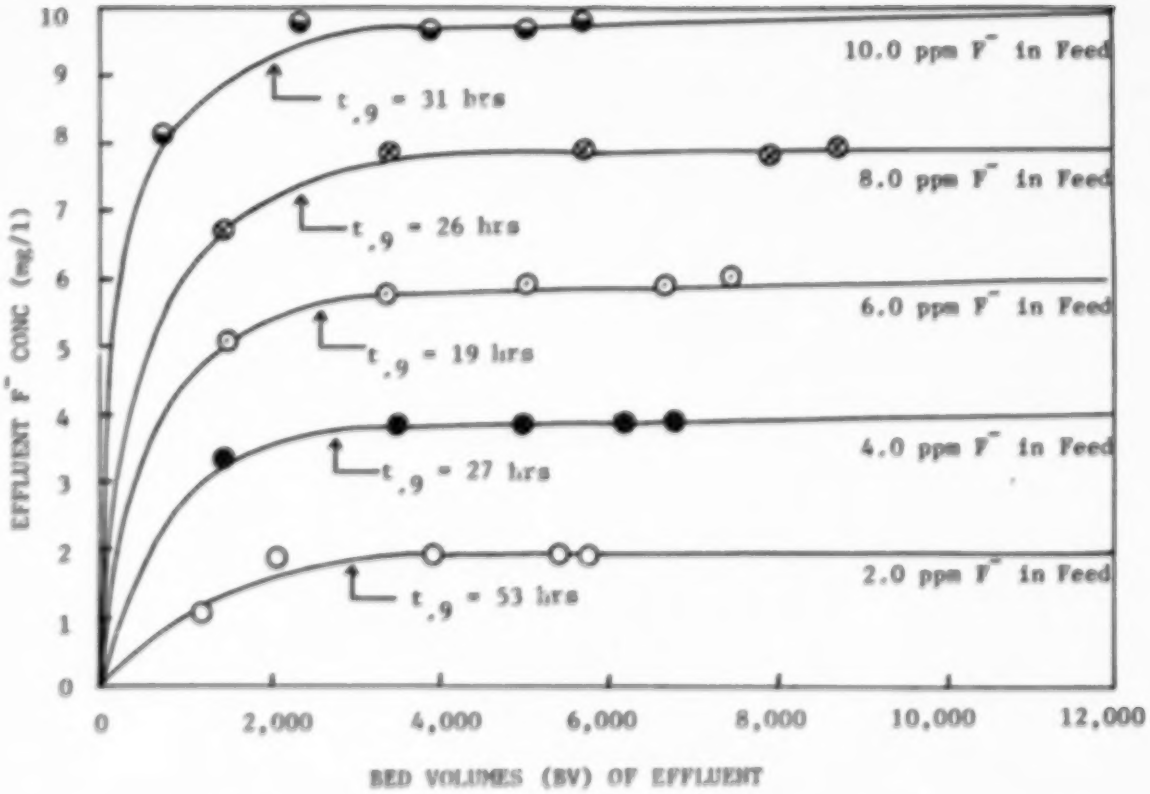


FIGURE A6 MINI-COLUMN EFFLUENT CONCENTRATION HISTORIES, pH = 8.0
EFFECT OF CONCENTRATION ON COLUMN KINETICS
Q = 1.23 ml/min, EBCT = .81 min, BV = 1.0 ml
$t_{.9}$ = time to 90% of equilibrium in hours

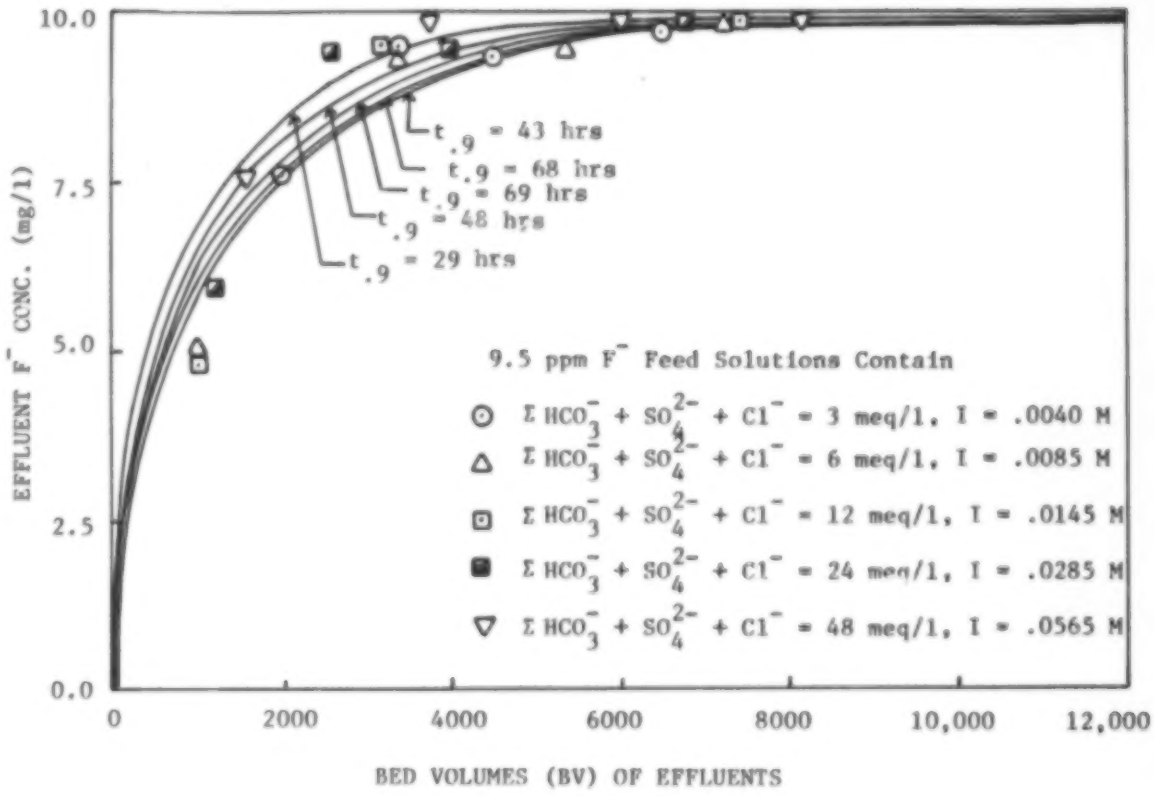

10.0
7.5
5.0
2.5
0.0
EFFLUENT F⁻ CONC. (mg/l)
0
2000
4000
6000
8000
10,000
12,000
BED VOLUMES (BV) OF EFFLUENTS
t.9 = 43 hrs
t.9 = 68 hrs
t.9 = 69 hrs
t.9 = 48 hrs
t.9 = 29 hrs
9.5 ppm F⁻ Feed Solutions Contain
Σ HCO3⁻ + SO4²⁻ + Cl⁻ = 3 meq/l, I = .0040 M
Σ HCO3⁻ + SO4²⁻ + Cl⁻ = 6 meq/l, I = .0085 M
Σ HCO3⁻ + SO4²⁻ + Cl⁻ = 12 meq/l, I = .0145 M
Σ HCO3⁻ + SO4²⁻ + Cl⁻ = 24 meq/l, I = .0285 M
Σ HCO3⁻ + SO4²⁻ + Cl⁻ = 48 meq/l, I = .0565 M

FIGURE A7 MINI-COLUMN EFFLUENT CONCENTRATION HISTORIES, pH = 7.1
EFFECT OF IONIC STRENGTH ON COLUMN KINETICS
Q = 1 ml/min, EBCT = 1 min, BV = 1.0 ml
$t_{.9}$ = time to 90% of equilibrium in hours

GLOSSARY

"as $CaCO_3$": Normality (N) can be converted to calcium carbonate equivalents. There are 50 mg of $CaCO_3$ per milliequivalent.

bed: Alumina resin contained in a column. Water to be defluoridated by alumina adsorption process is passed downward through the column

breakthrough: The point at which F^- concentration in the effluent reaches the MCL or some predetermined concentration.

elution: Application of NaOH solution to an exhausted alumina bed so as to "elute" or drive off the adsorbed anions.

exhaustion: The step in an adsorption cycle in which the undesirable F^- ions are removed from the water, and are adsorbed on alumina bed.

ion-exchange: A physicochemical process in which ions in the water being treated replace and are exchanged for ions in a solid phase (alumina).

isotherm: A constant temperature plot of resin phase concentration of an ion versus the water phase concentration of that ion, at the equilibrium slope.

milliequivalent (meq): 1/1000 of a gram equivalent of ion.

regeneration: Restoration of the activated alumina after exhaustion to reclaim its original adsorption capacity.

selectivity: A measure of the relative affinity for one ion over another exhibited by the alumina. Selectivity is measured by the separation factor.

separation factor (binary): The ratio of the distribution of ions between the solid phase and the liquid phase at equilibrium.

$$\alpha_B^A = \frac{\text{distribution of A ions between solid \& liquid phase}}{\text{distribution of B ions between solid \& liquid phase}}$$

$$= \frac{y_A/x_A}{y_B/x_B} = \frac{q_A/Q_T \times C_T/C_A}{q_B/Q_T \times C_T/C_B}$$

superficial detention time (t): The time a particle of feed water spends in the empty alumina bed assuming plug flow. It is calculated as the empty

bed volume divided by the feed flow rate.

throughput: Ratio of the total amount of fluoride which comes in contact with the adsorption column during a specified amount of time to the total adsorptive capacity of the column.